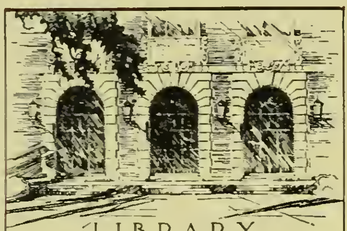

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~~CHEMISTRY~~

AMERICAN

College

CHEMICAL JOURNAL

EDITED BY

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VOL. 4. 1882-83.

BALTIMORE : THE EDITOR.

ISAAC FRIEDENWALD, PRINTER,
103 W. Fayette St.

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THE ANALYLSIS OF IRON ORES CONTAINING BOTH PHOSPHORIC AND TITANIC ACIDS.[1]

By Thomas M. Drown and P. W. Shimer.

The precipitation of phosphoric with titanic acid by boiling an iron solution which had been reduced to the ferrous condition by sulphuretted hydrogen or sulphurous acid was first noticed by E. H. Bogardus in 1874.[2] Since that time, as far as we are aware, not much has been published on the relation of these two acids to each other, and to silicic acid in the ordinary course of analysis of iron ores. The following investigation may perhaps aid in clearing up some of the obscure points in the analysis of titaniferous ores.

The Determination of Phosphorus.

From two to five grams of the finely powdered ore are weighed into a beaker and treated with about 50 cc. of hydrochloric acid (sp. gr. 1.12), evaporated to dryness, and heated in an air-bath for an hour to 110° to 120° C. To the dry mass are added 50 cc. of hydrochloric acid (1.12), and the solution filtered off from the insoluble residue. On washing this residue with water the filtrate often runs through turbid. This can be avoided by washing with dilute nitric acid, or, better, with an acid solution of ammonium nitrate. The filtrate contains the greater part of the phosphoric acid, but the residue may contain a notable amount.

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[1] Read before the American Institute of Mining Engineers.

[2] American Journal of Science, III. 8, 334.

Treatment of the Residue.—Fuse the residue with sodium carbonate and extract with water. Sodium phosphate and silicate go into solution and sodium titanate remains insoluble. Filter, acidify the filtrate with nitric acid, evaporate to dryness, moisten with nitric acid, and dissolve in water. Filter from the silica, concentrate the filtrate, neutralize nearly with ammonia, and precipitate with ammonium molybdate. This is the best method of separating the phosphorus from the insoluble residue. The bulk of the phosphorus may, however, be extracted from the moist residue by washing with ammonia.

Treatment of the Filtrate.—Evaporate to a small bulk, and add enough nitric acid to drive off all the hydrochloric acid on evaporation. If the concentrated solution is clear, add ammonia until a slight permanent precipitate is formed; redissolve this in a few drops of nitric acid, and add ammonium molybdate solution.

In the ores of which we are speaking, a precipitate generally separates on evaporating to a small bulk. The addition of more nitric acid with continued heat often redissolves this; in this case, the evaporation must not be carried too far, or the substance will again precipitate. This precipitate contains phosphoric acid and titanic acid. If it is impossible to get it into solution in nitric acid, it must be filtered off and washed with ammonium nitrate solution. It is then ignited, fused with sodium carbonate, extracted with water, and the filtrate, after acidifying with nitric acid, precipitated with molybdate solution.

After the addition of the ammonium molybdate to the main solution, as mentioned above, it is heated rather hot, say from 50° to 70° C., for half an hour, with frequent vigorous stirring. The precipitate is usually allowed to stand over night, but if filtered within two hours, there will be no appreciable amount of phosphorus unprecipitated. The yellow precipitate is filtered off and washed well with a mixture of 325 cc. of nitric acid (sp. gr. 1.2), 100 cc. of ammonium hydrate (sp. gr. 0.96), and 100 cc. of water. It is then dissolved upon the filter in dilute ammonia. The solution will probably run through turbid, and a gelatinous residue will remain in the filter. The solution is heated for some time and filtered, and this residue, which contains both phosphoric and titanic acid, is treated, together with the gelatinous residue insoluble in ammonia, with nitric acid, and the resulting solution precipitated with ammonium molybdate. By heating and stirring, the phosphoric acid can be completely precipitated in an hour, so that it will not retard the analysis materially. The solution of this yellow precipitate in ammonia is to be added to the main ammoniacal solution, and magnesia mixture added with the usual precautions. By active stirring after the addition of magnesia mixture the complete precipitation of the phosphoric acid may be effected in an hour or two.[1] In the analysis of an ore containing 4.74 per cent. of phosphoric acid (mostly as apatite) and 0.65 per cent. of titanic acid, the phosphoric acid was found (in duplicate analyses) as follows:

	I.	II.
Phosphoric acid in the hydrochloric acid solution,	4.370	4.330
Phosphoric acid in the residue insoluble in hydrochloric acid,	0.280	0.390
Phosphoric acid in the precipitate which separated from the solution of the yellow precipitate in ammonium hydrate,	0.016	0.02
Total,	4.666	4.747

Determination of the Titanic Acid.

One to two grams of the finely powdered ore are weighed into a large platinum crucible. Potassium bisulphate[2] to the amount of 12 to 15 times the weight of the ore is next weighed out in another vessel. Mix the ore in the bottom of the crucible with about one-quarter of the bisulphate, and fuse until the excess of sulphuric acid is nearly all driven off. During the progress of the fusion, the lid must be lifted a very little at short intervals, in order to watch the state of the fusion. It should not be allowed to rise above two-thirds the height of the crucible. Add now another quarter of the bisulphate, and heat again as before, until nearly all the excess of the sulphuric acid is driven off. Then add the remaining half of the bisulphate, and heat until the whole mass is in quiet fusion. Too much sulphuric acid should not be driven off at this stage, or the subsequent solution in water will be retarded. The fused mass may be poured out into a large platinum dish, or it may be removed from the crucible in one lump by inserting a stout piece of platinum wire while still soft, and allowing the mass to solidify about it. A gentle heat on the outside of the crucible will quickly loosen the mass, which may now be lifted out easily. The former method is preferable, because of the thinness of the mass and its readier solubility.

---

[1] The action of stirring or other agitation in hastening precipitation, although well known, is not, I think, as often made use of in analysis as it might be.

[2] In order to make a successful determination of titanic acid, it is necessary to have good potassium bisulphate. This can seldom be bought in a condition fit for use. It usually contains water; sometimes an excess of sulphuric acid; it also usually contains an insoluble siliceous residue. To prepare it for use, it is dissolved in water and filtered, the solution evaporated to dryness, and fused until all the water is driven off and the mass is in quiet fusion. It is sometimes necessary to drive off some sulphuric acid. It is then powdered for use. Bisulphate thus prepared will not mount readily in the crucible, and a quiet fusion at a red heat can be obtained.

When the mass has become cold, it is dissolved in plenty of cold water. This usually requires at least twelve hours. When it is evident that all has dissolved but silica and silicates,[1] filter into a large beaker. This insoluble residue should, after ignition, be again fused with bisulphate and tested as below for titanic acid. To the main solution we add sodium carbonate solution until a slight permanent precipitate is obtained, then 3 to 4 cc. of sulphuric acid of 1.23 sp. gr. This redissolves the slight precipitate and makes the solution sufficiently acid.

Add now sulphurous acid in excess, and dilute largely with water (1 to 1.5 liter); cover with a watch-glass, and boil about two hours, adding sulphurous acid solution and water as the evaporation goes on.

The titanic acid is precipitated, and with it phosphoric acid and oxide of iron. Filter hot (best done by means of a siphon), and wash with hot water. This precipitate of titanic acid and phosphoric acid is not finely granular like that of pure titanic acid, but is flocculent, and shows no tendency to run through even a very porous filter. It is dried, ignited, and weighed. In spite of the fact that it contains a very notable amount of iron, it is usually white after ignition. It is fused with sodium carbonate and extracted with water. Sodium titanate and oxide of iron remain insoluble, while sodium phosphate goes into solution. The residue is dissolved in sulphuric acid (sp. gr. 1.23), filtered, neutralized with sodium carbonate, 2 to 3 cc. of sulphuric acid added, and then sulphurous acid as above. The titanic acid precipitated from this solution is free from phosphoric acid and iron.

If, instead of fusing the first precipitate of titanic acid with sodium carbonate, it is re-fused with potassium bisulphate, there will remain on treatment with cold water an isoluble residue containing titanic acid and phosphoric acid.

---

[1] In ores containing lime, calcium sulphate is often found in this insoluble residue.

The following analytical results will illustrate the foregoing description:

	I.	II.
First precipitate of titanic acid containing phosphoric acid and iron (in duplicate), per cent.	3.18	2.40

No. 1 was fused with sodium carbonate and treated with water as above. It consisted of

Titanic acid,	0.65
Phosphoric acid,	1.60
Sesquioxide of iron,	.84
Loss,	.09
	3.18

No. 2 was fused with potassium bisulphate, and gave:

Residue insoluble in cold water,	1.83
Precipitate by boiling the solution.	.34
Sesquioxide of iron, by difference,	.23
	2.40

The titanic acid precipitated by boiling (.34) contained both phosphoric acid and iron.

The residue insoluble in cold water (1.83) was fused with sodium carbonate as described above; it gave:

Phosphoric acid,	.96
Titanic acid,	.42
Sesquioxide of iron, by difference,	.45
	1.83

The precipitate by boiling (.34), similarly treated, gave:

Phosphoric acid,	.05
Titanic acid,	.12
Sesquioxide of iron, by difference,	.17
	.34

The complete analysis of the original precipitate (2.40) thus shows:

Titanic acid,	.54
Phosphoric acid,	1.01
Sesquioxide of iron, by difference,	.85
	2.40

The titanic acid is here doubtless 10 per cent. too low, owing to the many fusions and precipitations to which it was subjected.

Determination of Iron.

If the ore contains less than one per cent. of titanic acid, no appreciable error will result from neglecting it. If it contains more than this, the iron must be determined in the filtrate from the titanic acid. The first precipitation of titanic acid contains iron. This is separated by the sodium carbonate fusion, and may be added to the main solution after separation of the titanic acid. The iron is then determined by reduction with zinc and titration with permanganate.

Determination of Silica and Alumina.

When an iron ore containing phosphoric and titanic acids is treated for silica by the usual method (fusion with sodium carbonate, solution in dilute hydrochloric acid, evaporation to dryness, and separation of silica at 110° C., solution in hydrochloric acid and water, and filtration from the insoluble residue), the siliceous residue consists of silica, titanic acid, phosphoric acid, and iron. In the case of an ore containing 3.50 per cent. of silica, this residue (which, in spite of the iron in it, is white after ignition) amounted to 6.11 per cent. The presence of phosphoric acid and iron with the silica of course renders worthless the estimation of alumina by difference.

Before speaking of the determination of the silica, we will consider how we may get the phosphoric acid and iron into the main solution where they belong. The insoluble residue (containing silica, titanic acid, phosphoric acid, and iron) is fused with sodium carbonate, and extracted with water. Sodium phosphate and silicate dissolve, and sodium titanate and ferric oxide remain behind. Acidify the filtrate with hydrochloric acid, and evaporate to dryness; take up with hydrochloric acid and water, and filter off the silica; add the filtrate to the solution to be precipitated by sodium acetate. Dissolve the residue insoluble in water (containing the sodium titanate and ferric oxide) in sulphuric acid, and separate the titanic acid from the iron by boiling, as usual. Filter from the titanic acid, and add bromine-water to the filtrate, in order to oxidize the iron, boil, and precipitate the iron with ammonia. Filter and weigh it with the precipitate of iron, alumina, and phosphoric acid, separated as basic acetate.

Some titanic acid may go into the filtrate, which is to be precipitated by sodium acetate. In this case it will contaminate the precipitate of iron, alumina, and phosphoric acid. It is therefore necessary, after this precipitate has been weighed, to grind it in an agate mortar, and weigh out accurately as much of it as possible, fuse with potassium bisulphate, and determine the titanic acid in it by boiling, etc. The titanic acid thus found is to be deducted from the weight of the original precipitate. There will not in all cases be titanic acid in this precipitate, but it is not safe to omit testing for it.

The silica may also be determined by fusing the residue from the second bisulphate fusion for titanic acid with sodium carbonate, and separating the silica, as usual. Or it may be determined by fusing 1 to 1.5 gram of the ore with sodium carbonate, dissolving in hydrochloric acid, and adding an excess (50 cc.) of sulphuric acid (1.23), and evaporating until all the hydrochloric acid is driven off. This renders the silica insoluble. By now dissolving the ferric sulphate in a large excess of hydrochloric acid by aid of heat, everything goes into solution but the silica. When this point is reached, it is known by the absence of everything but transparent gelatinous silica floating in flocks in the clear solution. Calcium sulphate may contaminate the silica, if the ore contains much lime; but it does not look like gelatinous silica, and dissolves on dilution with water.

The following determinations illustrate the foregoing description:

	I.	II.
Insoluble in hydrochloric acid,	6.11 per cent.	5.38 per cent.

Fused with sodium carbonate and extracted with water, solution contained:

I.		II.	
Silica, ...	3.31	Silica, . . .	3.63
Phosphoric acid, . .	1.03	Phosphoric acid, . .	.71

Residue contained:

I.		II.	
Titanic acid, . . .	.65	Titanic acid, . . .	.65
Sesquioxide of iron, . .	1.33	Sesquioxide of iron, . .	.58

Totals.

	I.	II.
Silica, ...	3.31	3.63
Phosphoric acid, ...	1.03	.71
Titanic acid, ...	.65	.65
Sesquioxide of iron, ...	1.33	.58
	6.32	5.57

	I.	II.	III.
Silica made insoluble by sulphuric acid,	3.40	3.48	3.54
Silica from residue insoluble in bisulphate,	3.70	3.74	..
Residue insoluble in bisulphate, . .	4.91	5.03	..

THE CONDITION OF SULPHUR IN COAL, AND ITS RELATION TO COKING.[1]

BY THOMAS M. DROWN.

At the meeting of the Institute in New York, in February, 1880,[2] I described a process of determining sulphur in metallic sulphides with especial reference to the determination of pyrites in coal. The process, as then described, is as follows: A solution of sodium hydrate, of 1.25 specific gravity, is saturated with bromine. If an excess of bromine is used it must be neutralized by the addition of a little more sodium hydrate. The pulverized mineral or coal is moistened with 25 cc. of this solution and heated, then hydrochloric acid is added cautiously to just acid reaction. This operation is repeated with another 25 cc. of the alkaline solution, and again rendered acid. The mixture should be kept hot. The contents of the beaker or dish are then evaporated to dryness to separate silica and taken up by dilute hydrochloric acid. The sulphuric acid is precipitated, with the usual precautions, by barium chloride. In the paper referred to, determinations by this process of sulphur in coal were given, which, although agreeing closely with one another, yet fall far short of the total sulphur in the coal, and the inference was that the sulphur not oxidized by the treatment with the bromine solution was an organic constituent of the coal, and could only be determined by a process which would oxidize the coal completely.

I am now able to give further results of the application of this process to the analysis of coal and coke. The object in view in this investigation was to determine, if possible, the effect of coking on the amount and condition of sulphur in the coal. Although the results in this regard are not as decisive as could be wished, yet many interesting facts have been noticed in the course of the work.

The coals used were from Pennsylvania and Virginia and will be simply designated by letters. Two series of experiments were made. In the first the coke was made in the laboratory, in platinum crucibles; and in the second, "industrial coke," made in beehive ovens, was used.

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[1] Read before the American Institute of Mining Engineers.

[2] This Journal, **2**, 401; and Transactions of the American Institute of Mining Engineers, **8**, 569.

In the first series the total sulphur was determined, by way of control, by fusion with alkaline carbonates and nitre; and in the second, by Eschka's method of heating the coal with calcined magnesia and sodium carbonate.

First Series.

COAL A.

Proximate Analysis.		Analysis of Ash.	
Moisture . .	0.75	Silica, . . .	47.74
Volatile matters, .	15.35	Alumina and oxide of iron,	34.17
Fixed carbon, .	66.10	Lime, . . .	7.61
Ash, . . .	17.80	Magnesia, . .	0.98
		Sulphuric acid .	5.30
	100.00		95.80

The small quantity of ash used for this analysis is doubtless the cause of the imperfect result.

SULPHUR DETERMINATIONS IN COAL A.

I. By Bromine Mixture.	II. In residue from I. by combustion in oxygen, and absorption by solution of potassium permanganate.	III. In Ash from II. by fusion with sodium carbonate.	IV. Total, sum of I., II., and III.	V. By direct combustion of coal in oxygen, and absorption by solution of potassium permanganate.	VI. In Ash from V. by fusion with sodium carbonate.	VII. Total, sum of V. and VI.	VIII. Total by fusion with sodium carbonate and nitrate.
1.660	0.640	0.040	2.340	1.983	0.203	2.186	1.940
1.640	0.520	0.043	2.203	1.768	0.329	2.097	1.980
1.670	0.563	0.026	2.259	1.942	0.212	2.154	

SULPHUR DETERMINATIONS IN COKE A.

1.073	0.747	0.065	1.885	1.287	0.477	1.764	..
1.180	0.666	0.062	1.908	1.290	0.494	1.784	..
1.180	0.627	0.045	1.852	..	..	..	..

COAL B.

Proximate Analysis.	
Moisture, . .	3.48
Volatile matters, .	25.55
Fixed carbon, .	66.63
Ash, . . .	4.34
	100.00

Analysis of Ash.	
Silica, . . .	28.89
Alumina and oxide of iron,	65.92
Lime, . . .	2.49
Magnesia, . .	0.57
Sulphuric acid, .	2.02
	99.89

Sulphur Determinations in Coal B.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
By Bromine Mixture.	In residue from I. by combustion in oxygen, and absorption by solution of potassium permanganate.	In Ash from II. by fusion with sodium carbonate.	Total, sum of I., II., and III.	By direct combustion of coal in oxygen, and absorption by solution of potassium permanganate.	In Ash from V. by fusion with sodium carbonate.	Total, sum of V. and VI.	Total by fusion with sodium carbonate and nitrate.
0.041	0.450	0.031	0.522	0.431	0.058	0.489	0.474
0.035	0.464	0.037	0.536	0.461	0.035	0.496	0.373
..	..	..	..	0.454	0.053	0.507	..

Sulphur Determinations in Coke B.

0.034	0.406	0.060	0.500	0.429	0.087	0.516	0.495
0.056	0.400	0.063	0.519	0.441	0.080	0.521	0.536

COAL C.

Proximate Analysis.	
Moisture, . .	1.16
Volatile matters, .	33.08
Fixed carbon, .	61.81
Ash, . . .	3.95
	100.00

Analysis of Ash.	
Silica, . . .	60.94
Alumina and oxide of iron,	32.86
Lime, . . .	1.75
Magnesia, . .	0.10
Sulphuric acid, .	2.28
	97.93

SULPHUR DETERMINATIONS IN COAL C.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
By Bromine Mixture.	In residue from I. by combustion in oxygen, and absorption by solution of potassium permanganate.	In Ash from II. by fusion with sodium carbonate.	Total, sum of I., II., and III.	By direct combustion of coal in oxygen, and absorption by solution of potassium permanganate.	In Ash from V. by fusion with sodium carbonate.	Total, sum of V. and VI.	Total by fusion with sodium carbonate and nitrate.
0.127	0.647	0.028	0.802	0.693	0.036	0.729	0.766
0.139	0.631	0.022	0.792	0.701	0.030	0.731	0.712
..	..	.	..	0.762	0.035	0.797	..

SULPHUR DETERMINATIONS IN COKE C.

0.041	0.547	0.026	0.614	0.583	0.033	0.616	0.640
0.018	0.582	0.028	0.628	0.605	0.034	0.639	0.650

It has been recently stated by Mixter[1] that bromine-water, or a solution of bromine in hydrochloric acid, fails to oxidize all the sulphur dioxide produced by the combustion of coal, and that the vapors should be carried into a large bottle containing bromine vapors before they are allowed to escape. I have found also that a final large bromine bottle collects a very small amount of sulphuric acid after the vapors have passed through a solution of potassium permanganate. A coal containing 0.721 per cent. of sulphur gave 0.009 per cent. in the large bromine bottle, and another coal containing 0.605 per cent. gave 0.024 per cent. In the following experiments the large bromine bottle was used, and the sulphur given as absorbed by permanganate solution includes the small amount found in the bromine bottle. As stated in a previous paper, I much prefer potassium permanganate to bromine for the oxidation of sulphur dioxide or sulphuretted hydrogen.

In the combustion of bituminous coals in oxygen explosions frequently occur. These may be avoided by simply diluting the oxygen with atmospheric air to the extent of equal volumes. The coal or coke can be best ignited in the tube in the following manner. The platinum boat containing the coal is placed just within the tube, which is then filled with oxygen. The cork is then removed, and a glowing splinter of charcoal placed in the end of the boat, which is quickly pushed in the middle of the tube. The flow of oxygen is at once resumed and the coal continues to glow until it is all consumed. The gas in the combustion-furnace is kept turned low until the coal is nearly consumed, when it is turned on to a good red heat.

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[1] This Journal, 2, 396.

In the foregoing experiments the coke was made in platinum crucibles over a Bunsen burner. To test the effect of coking on an industrial scale, I had samples taken of the coal which was put into an oven and of the coke which came out. This was not done under my supervision, and consequently some uncertainty exists as to the thoroughness of the sampling. The following are the results obtained on three samples of coal and the corresponding coke made in ovens.

The total sulphur was directly determined in these coals and cokes by Eschka's method of heating with calcined magnesia and sodium carbonate, and oxidizing the solution in water by bromine. This is much to be preferred, in regard to simplicity and accuracy, to fusion with alkaline carbonates and nitre.

Second Series.

COAL E.

Proximate Analysis.

Volatile matters (including moisture),	24.25
Fixed carbon,	70.51
Ash,	5.24
	100.00
Ash in coke,	5.41

The ash determinations in this coal and coke indicate imperfect sampling.

SULPHUR DETERMINATIONS IN COAL E.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
By Bromine Mixture.	In residue from I. by combustion in oxygen.	In Ash from II.	Total.	Direct combustion in oxygen.	In Ash from V.	Total.	Total by Eschka's method.	Iron.
0.155	0.488	0.020	0.663	0.721	0.044	0.765	0.733	0.32
0.156	0.478	0.017	0.651	0.679	0.032	0.711	..	..

SULPHUR DETERMINATIONS IN COKE E.

0.119	0.532	0.012	0.663	0.637	0.021	0.658	0.665	..
0.125	0.533	0.013	0.671	0.669	0.017	0.686	..	..

COAL F.

Proximate Analysis.

Volatile matters (including moisture), . .	29.75
Fixed carbon, ...	62.37
Ash, ...	7.88
	100.00
Ash in coke, ...	9.80

SULPHUR DETERMINATIONS IN COAL F.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
By Bromine Mixture.	In residue from I. by combustion in oxygen.	In Ash from II.	Total.	Direct combustion in oxygen.	In Ash.	Total.	Total by Eschka's method.	Iron.
0.349	0.560	0.014	0.923	0.923	0.045	0.968	0.949	0.666
0.354	0.546	0.012	0.912	0.905	0.043	0.948	..	..

SULPHUR DETERMINATIONS IN COKE F.

0.296	0.619	0.012	0.927	0.907	0.017	0.924	0.917	..
0.299	0.607	0.008	0.914	0.913	0.024	0.937	..	..

COAL G.

Proximate Analysis.

Volatile matters (including moisture), . .	38.01
Fixed carbon, ...	56.27
Ash, ...	5.72
	100.00
Ash in coke, ...	8.76

SULPHUR DETERMINATIONS IN COAL G.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
By Bromine Mixture,	In residue from I. by combustion in oxygen.	In Ash from II.	Total.	Direct combustion in oxygen.	In Ash from V.	Total.	Total by Eschka's method.	Iron.
0.129	0.588	0.018	0.735	0.749	0.042	0.791	0.759	0.290
..	..	..	..	0.727	0.045	0.772	..	..

SULPHUR DETERMINATIONS IN COKE G.

0.085	0.516	0.025	0.626	0.581	0.050	0.631	0.597	..
..	..	..	..	0.605	0.016	0.621	0.590	..

I add an analysis of anthracite, illustrating this method of treatment.

ANTHRACITE.

Analysis of Ash. (5.11 *per cent.*)

Silica, ...	50.06
Alumina and Iron, ...	44.22
Lime, ...	1.39
Magnesia, ...	0.21
Sulphuric acid, ...	2.05
	97.93

SULPHUR DETERMINATIONS IN ANTHRACITE.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
By Bromine Mixture.	In residue from I, by combustion in oxygen.	In Ash from II.	Total.	Direct combustion in oxygen.	In Ash from V.	Total.	Total by fusion with sodium carbonate and nitrate.
0.08	0.485	0.024	0.589	0.512	0.042	0.554	0.589
..	..	..	..	0.534	0.040	0.574	..

No calcium sulphate was found in any of these coals. They were tested by boiling for some time the finely pulverized coal with water slightly acidulated with hydrochloric acid, in a flask from which the air was excluded by a current of carbon dioxide. The precaution of excluding the air is necessary, since pulverized iron pyrites boiled with water (or solution of sodium carbonate, as has been recommended for the determination of calcium sulphate) with access of air is readily oxidized, and the water reacts for sulphuric acid.

In the second series of analyses it will be seen that there is in each case an excess of total sulphur over what is necessary to form pyrites with the iron, and that there is not enough sulphur, as determined by bromine, to form pyrites with all the iron. This would seem to indicate that the sulphur is present in these coals, both as pyrites and as an organic constituent of the coal, and also that the iron is present, both in combination with the sulphur and with silica or other inorganic constituents of the ash.

The foregoing determinations, while they are insufficient to throw much light on the effect of coking on the condition, or the elimination of sulphur in coal, may not be without value in indicating a new line of investigation of coals and cokes.

In the coal A, which contains sulphur in considerable amount, both as metallic sulphide and as an inherent constituent of the coal, and which, at the same time, is low in volatile ingredients, it would seem as if the elimination of sulphur was limited to a portion of that existing as pyrites, and that the organic sulphur, if we may so call it, was not affected by the process of coking. This becomes apparent if the percentage of sulphur in the coke is calculated on the basis of the amount of coal required to make the coke.

In the other coals, low in pyrites and higher in volatile matters, there was an elimination of the organic surphur to the extent of 20 to 45 per cent. It would be interesting to determine the effect of different methods of coking, and of the duration of the process on this elimination.

If we admit the presence of organic sulphur in coke, it is probable that no plan for its removal could be effective which would not involve the destruction of the coke itself. In the method of analysis given, we are able to distinguish between the organic and inorganic combinations of sulphur in coke, and thus to determine the feasibility of its desulphurization.

It is interesting to note (more especially in coal A) that the ash of the coal which has been burned directly in oxygen contains much more sulphur than that from the same coal which has had its sulphur, in the form of pyrites, removed by bromine.

The analytical determinations in this investigation were made with great care by Mr. P. W. Shimer.

ON THE COMPOSITION OF AMERICAN GRASSES.

By Clifford Richardson.

The large number of analyses of grasses which have been made during the last few years in the laboratory of the Department of Agriculture make it possible to deduce certain averages for their composition which are of great interest, both in comparison with those of Wolff for German grasses, and as showing the relations of cultivated and wild grasses toward each other, and the variations in composition which one species may present when grown on different soils and in different climates.

In the following tables are presented the figures which I have obtained:

TABLE I.

AVERAGE COMPOSITION OF GRASSES IN BLOOM.

	AMERICAN.				GERMAN.		
	77 Analyses of Wild Grass.	21 Analyses of Grasses from one farm in Penn.	19 Analyses of Grasses from Dept. Grounds.	6 Analyses of Orchard Grass from Various Localities.	Wolff's Averages.		
					Fair.	Good.	Very Good.
Ash.............	7.90	7.95	7.44	7.38	6.30	7.23	8.24
Fat.............	2.90	3.12	3.52	3.33	2.34	2.92	3.29
N free Extract....	53.90	55.75	55.82	55.17	46.53	47.84	48.93
Crude Fibre	27.10	23.14	22.47	25.19	34.09	30.69	25.77
Nitrogen × 6.25..	8.20	10.04	10.25	8.91	10.74	11.32	13.77
P.c. N as Nonalb..	34.7	30.1	18.3	25.2	..	..	..
Nutritive Ratio...	1 : 10.2	1 : 8.1	1 : 8.0	1 : 9.4	1 : 7.7	1 : 7.2	1 : 5.7

It is plainly shown that all our American grasses are strikingly different in composition from similar German varieties. In the first place the content of nitrogen is smaller, accompanied by a largely decreased amount of fibre. In the next place, these changes are made up by a larger amount of nitrogen free extract and a slight increase in fat. The nutritive ratio, then, is much wider than in the German grasses.

Considering the relations of the different kinds of American grasses to each other, it is apparent that the wild varieties are, as would be expected, of much less nutritive value than those which have been cultivated. The average composition of orchard grass is not equal to that of the better cultivated varieties; and among the latter, the higher the cultivation the better the quality, as is shown by the averages for the grasses grown in Pennsylvania, which had not been as highly fertilized as those from the grounds of the Department of Agriculture in Washington. The explanation of the differences between American and German grasses may be that the latter have been under cultivation so much longer that they have improved in quality; or rather, perhaps, that they grow on more highly fertilized soils from which they are able to assimilate larger amounts of nitrogen; the grasses, as is well known, being quite dependent on the soil for that element, while they are, owing to their larger content of fibre, perhaps of less real value than the American species. In this connection it would be most interesting to study the effect of different fertilizers on our native and cultivated species, and such a course of experiment I intend to carry out in the near future. Another prominent fact which is shown by the table is, that in the wild grasses the amount of nitrogen in the non-albuminoid form is larger than in the better varieties, and that the amount varies somewhat as the quality of the grass, the more highly cultivated varieties from the grounds of the Agricultural Department having only a little more than half as much as is found in the wild species. The character of the soils upon which the specimens grew which I have analyzed may have had some influence upon the results, outside of the amount of cultivation to which they were subjected. The wild grasses were for the greater part from the sandy soils of the South; those from Pennsylvania grew upon a micaceous loam, and the soil of the grounds of the Department of Agriculture is of a heavy nature, as indicated by an analysis in the report for 1879, p. 93.

In this connection the variations in the composition of a single species when grown in different localities is of interest, and in Table II. may be seen the changes which have been observed in *Dactylis.*

TABLE II.

ANALYSES OF *Dactylis Glomerata* [ORCHARD GRASS] FROM VARIOUS LOCALITIES.

EARLY BLOOM.

LOCALITY.	Ash.	Fat.	N. Free Extract.	Crude Fibre.	Nitrogen × 6.25.	Total Nitrogen.	Non-albuminoid Nitrogen.	Per cent. of Total N. as Non-alb.
District of Columbia	8.64	3.98	50.20	24.67	12.51	1.99	.70	38.7
North Carolina....................	8.90	3.68	52.16	24.97	10.29	1.61	.63	39.1

FULL BLOOM.

	Ash.	Fat.	N. Free Extract.	Crude Fibre.	Nitrogen × 6.25.	Total Nitrogen.	Non-albuminoid Nitrogen.	Per cent. of Total Nit. as Non-alb.
North Carolina	7.42	3.56	56.03	23.08	9.91	1.58	.30	19.0
District of Columbia	8.07	3.24	53.76	25.40	9.53	1.53	.16	10.5
Maine	8.02	3.39	54.80	26.05	8.74	1.40	.36	25.7
District of Columbia	6.00	3.62	57.34	24.42	8.62	1.38	.42	30.4
Pennsylvania	6.33	2.66	54.94	27.51	8.56	1.37	.51	37.2
New Hampshire	8.44	3.49	54.75	24.91	8.41	1.35	.42	30.9
Average Early Bloom	8.77	3.83	51.18	24.82	11.40	1.80	.70	39.9
Average Full Bloom	7.38	3.33	55.19	25.19	8.91	1.43	.36	25.2

The specimens from the District of Columbia grew on a rather heavy soil similar to that before mentioned; those from North Carolina, on a light sandy soil; that from Maine, on a light loam; that from Pennsylvania, on a micaceous loam, and that from New Hampshire on a poor, loose loam; without much cultivation in any case, except the first two specimens in early and full bloom, from the District of Columbia and North Carolina.

Among these results it appears again strikingly that the amount of non-albuminoid nitrogen does not increase with an increase in the total amount of nitrogen in the grass, the poorer specimens having more than twice as much relatively to the total nitrogen than the more highly cultivated ones, owing to the fact that the absolute amount of non-albuminoid nitrogen does not vary within certain limits, the diminution of the total amount falling largely on the albuminoid forms. The variations in the non-nitrogenous elements of the plant do not show any regularity dependent on climate or surroundings, in the same way that the nitrogenous constituents do; and it is probable that a much larger number of analyses would be necessary to permit the drawing of conclusions in this direction.

The presence of non-albuminoid nitrogen in varying amount has been noted in the previous tables. In the following series of analyses of *Alopecurus pratensis*, Meadow Foxtail, which have been selected from a large series published in the report of the Department of Agriculture for 1880, the changes which take place in its relative amount, as well as those of the general constituents of the plant, are shown.

TABLE III.

ANALYSES OF *Alopecurus Pratensis* AT FOUR STAGES OF GROWTH.

CONSTITUENTS.	HEAD APPEARING.		BEFORE BLOOM.		IN BLOOM.		AFTER BLOOM.	
When cut	April	19th.	April	19th.	May	1st.	May	12th.
Water in fresh grass	77.1	..	76.7	..	60.0	..	60.6	..
AIR DRY SUBSTANCE.								
Water	8.75	8.75	9.83	9.83	7.70	7.70	8.58	8.58
Ash	8.40	8.40	7.12	7.12	7.15	7.15	7.47	7.47
Ether Extract	4.28	..	4.02	..	3.10	..	3.20	..
Soluble in Alcohol	..	3.40	..	3.07	..	2.25	..	2.35
Insoluble in Alcohol	..	.88	..	.95	..	.85	..	.85
80 per cent. Alcohol Extract	16.36	..	12.69	..	11.65	..	10.20	..
Insoluble in Water	..	1.46	..	1.75	..	1.53	..	1.24
Soluble in Water	..	..	..	..	..	..	..	..
Sugars	..	3.40	..	2.40	..	2.70	.	2.70
Organic Acids, &c	..	8.67	..	5.28	.	7.42	..	5.98
Amido Bodies	..	2.83	..	2.26	..	.00	..	.28
Water Extract	3.02	3.02	2.06	2.06	1.68	1.68	1.64	1.64
Acid Extract	15.70	15.70	20.50	20.50	21.60	21.60	20.50	20.50
Alkali Extract (Diff.)	16.24	16.24	15.33	15.33	15.19	15.19	17.74	17.74
Crude Fibre	16.62	16.62	20.20	20.20	21.95	21.95	23.18	23.18
Albumen	10.63	10.63	9.25	9.25	9.98	9.98	7.49	7.49
DRY SUBSTANCE.								
Ash	9.21	9.21	7.90	7.90	7.75	7.75	8.17	8.17
Ether Extract	4.69	..	4.46	..	3.36	..	3.50	..
Soluble in Alcohol	..	3.73	..	3.40	..	2.44	..	2.57
Insoluble in Alcohol	..	.96	..	1.05	..	.92	..	.93
N. Free Extract	52.16	..	51.66	..	54.30	..	54.35	..
80 per. cent. Alcohol Extract	..	..	..	..	..	..	..	..
Insoluble in Water	..	1.60	..	1.94	..	1.65	..	1.36
Soluble in Water	..	..	..	..	..	..	..	..
Sugars	..	3.73	..	2.66	..	2.92	..	2.95
Organic Acids, &c	..	9.50	..	5.86	..	8.04	..	6.54
Amido Bodies	..	3.10	..	2.50	..	.00	..	.34
Water Extract	..	3.31	..	2.28	..	1.82	..	1.79
Acid Extract	..	17.20	..	22.74	..	23.41	..	22.42
Alkali Extract (Diff.)	..	6.79	..	17.00	..	16.46	..	19.41
Crude Fibre	18.21	18.21	22.41	22.41	23.78	23.78	25.36	25.36
Albumen	..	11.76	..	10.26	..	10.81	..	8.19
Nitrogen × 6.25	15.73	..	13.53	..	10.81	..	8.62	..
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Total Nitrogen	2.52	..	2.17	..	1.73	..	1.33	..
N. as Albumen	1.86	..	1.64	..	1.73	..	1.26	..
N. as Non-Albuminoid	.66	..	8.53	..	.00	..	.07	..
Per cent. of N. as Non-Albumin'd	38.2	..	40.9	..	0.0	..	5.0	..
Nutritive Ratio	1 : 4.8	..	1 : 5.8	..	1 : 7.5	..	1 : 9.7	..

In this grass, which may be regarded as typical of most cultivated grasses, the changes which take place during its growth are represented in a short series of analyses, as it matures in a few weeks. The total nitrogen diminishes regularly from early to late stages. The albumen diminishes nearly in the same way, but remains constant for quite a long period at the time of blooming.

The non-albuminoid nitrogenous substances, while decreasing rapidly from the first stage at which the grass was collected to nothing at full bloom, increase again slightly after bloom. In many other grasses which I have analyzed this increase is much larger, and is very apparent. Among the non-nitrogenous constituents the fibre increases toward maturity while the fat decreases. Those substances which make up what is known as the "nitrogen free extract" in fodder analyses, while they do not present the same regularity of change as the previously mentioned constituents, show, in a few instances, a regular diminution or increase toward maturity. The sugars, or those substances extracted by alcohol and not precipitated by basic lead acetate, which reduce Fehling's solution, do not vary largely, but there is a larger amount in the young plant than in the other stages, contrary to what has been found in the sugar-producing grasses, sorghum and sugar cane. The organic acids, too, are present in larger amount in the young plant. A regular diminution takes place in the amount of gum, and a somewhat irregular increase in those indefinite substances extracted by acid and alkali. The conclusions which can be drawn from these results are perhaps better suited to an agricultural paper, and they will be passed over here.

In what forms the nitrogen of the grasses exists it is not possible at present to decide, but the following determinations, made with a specimen of *Dactylis glomerata* in one of the earlier stages of its growth, before the development of the panicle, gives some idea of what may be sought for.

TABLE IV.

Dactylis Glomerata before the Appearance of Panicle.

Forms of Nitrogen.

"Total nitrogen" (by soda lime)	2.40	2.38
N. soluble in water	.98	..
Soluble in 80 per cent. alcohol	.98	..
N. soluble in water and not precipitated by—		
tannic acid	.98	..
phosphotungstic acid	1.01	1.01
cupric hydrate	.84	.87
phosphomolybdic acid	.84	..
basic lead acetate	.84	.70
N. soluble in water and lactic acid and not precipitated by cupric hydrate	.73	.70
Nitric acid containing N	.099	..
Ammonia containing N	.093	..
Nitrogen as amides of amido acids	none.	

The forms of nitrogen which might occur in grasses are ammonia salts, nitrates, albumen, peptones, amides, amido-acids, alkaloids and carbamide bodies. The presence of albumen, ammonia salts and nitrates is shown by direct determination. The absence of alkaloids and peptones is shown by the fact that phosphotungstic and tannic acids do not precipitate anything from the water solution of the plant. That there are substances present in the water solution of the grass which are not precipitated by any of the reagents in the above table, points to the presence of amides or amido-acids. That the former are not present is shown by the fact that on boiling the aqueous extract with acids and then distilling with magnesia, no more ammonia is found than before the treatment with acid. The conclusion must be, then, that the non-albuminoid nitrogen of the plant exists as amido-acids, but of different kinds, as the different reagents do not all act uniformly in precipitating them, that is to say there is a substance precipitated by cupric hydrate which is not precipitated by tannic acid and phosphotungstate. It is probably an amido-acid forming difficultly soluble copper salts. Attempts to extract these nitrogenous bodies from a large amount of juice expressed from this grass were unsuccessful, owing to the presence of substances preventing crystallization.

WASHINGTON, *Dec.* 1881.

Contributions from the Chemical Laboratory of Harvard College.

XV.—AN INDIRECT DETERMINATION OF CHLORINE AND BROMINE BY ELECTROLYSIS.

BY LEONARD P. KINNICUTT.

In the indirect determination of chlorine and bromine the method most commonly employed is to precipitate both halogens with argentic nitrate, and then either to reduce the weighed argentic chloride and bromide to metallic silver by heating in an atmosphere of hydrogen, or to change the bromide into chloride by heating in a stream of chlorine gas.

The determination by either method is difficult, requires the closest attention, and is liable to give erroneous results; both on account of the slight loss that may occur in transferring the weighed chloride and bromide from the crucible to the glass tube, and also from slight volatilization during the heating. I have found that even in reducing the mixed haloids to metallic silver in a slow current of hydrogen, small particles of silver are almost always carried by the gas along the tube. Led by these facts, I attempted during the past winter to find a new method which would, if possible. from its accuracy and simplicity, tend to bring the indirect determination of chlorine and bromine when they occur in organic compounds more into vogue than is at present the case. In this attempt I believe I have been successful, and the method I have devised is based on the principle that melted argentic chloride and bromide are easily reduced to metallic silver by the galvanic current.

The details of the process are as follows:

After the mixture of the two halogen compounds of silver has been heated in a porcelain crucible so that they just fuse together, the crucible is cooled and weighed, a piece of platinum foil connected with a platinum wire is placed in the crucible so that it rests on the melted silver salts, and dilute sulphuric acid (1 pt. conc. to 3 pts. water by volume) is poured into the crucible until it is two-thirds full, a second piece of platinum foil united to a wire is then placed in the acid solution, care being taken that it does not touch the silver mixture. The zinc pole of a two-cell Bunsen battery is connected with the platinum foil that rests on the silver salts, and the carbon foil with the platinum foil just mentioned. The decomposition begins immediately, chlorine and bromine being given off from the positive electrode, the reduced silver remaining at the bottom of the crucible in the form of a porous mass. The reaction requires from twelve to eighteen hours; with a weight of less than one and a half gram of the mixed haloids I have found twelve hours sufficient to produce complete reduction; with a weight exceeding that amount I prefer to allow eighteen. When the argentic chloride and bromide are completely reduced, the battery is disconnected, the electrodes taken out of the sulphuric acid solution and washed with distilled water. The sulphuric is then poured off from the silver, and the silver is washed by decantation with distilled water, the decanted liquid being poured through a small filter; this is afterwards burnt, added to the silver sponge which still remains in the crucible; the crucible is then heated over a low free flame to constant weight. The weight thus found, minus the weight of crucible and filter ash, is of course the weight of silver contained in the argentic chloride and bromide.

The only point that requires any great degree of care in this process is the melting of the mixed haloids. The temperature at which the fusion takes place must be as low as possible, so as to avoid any volatilization, and the melted mass should be united as far as practicable in one piece.

In some of the following analyses I have used a platinum crucible. When this has been the case, one wire has been wound around the crucible, while the other, as before, has been merely allowed to dip into the acid solution; in this way the whole crucible serves as an electrode, and there is no need of bringing the melted chloride and bromide into one globule. With a platinum crucible, the washing of the reduced silver must be continued until a few drops of the filtrate gives no precipitate with baric chloride, and the drying should be done in an air bath at a temperature of about 150° C. After weighing, the silver, which always adheres to the crucible, can be dissolved out with dilute nitric acid.

The first series of analyses shows the accuracy of the process when either argentic chloride or bromide is taken alone, the second series when they occur together.

First Series of Analyses.

Wt. taken. Argentic chloride.	Wt. found. Silver.	Wt. calculated. Silver.
0.7206 grams.	0.5419 grams.	0.5425 grams.
1.2984 "	0.9771 "	0.9777 "
1.8455 "	1.3892 "	1.3889 "

Wt. taken. Argentic bromide.	Wt. found. Silver.	Wt. calculated. Silver.
0.9313 grams.	0.5352 grams.	9.5350 grams.
0.9421 "	0.5424 "	0.5424 "

In this connection I publish, by permission, three analyses, made according to this process, by Prof. J. P. Cooke, in determining the purity of a sample of argentic bromide.

	Wt. of argentic bromide.	Wt. of silver.	Per cent. of silver.
1.	4.1450 grams.	2.3817 grams.	57.444
2.	1.8172 "	1.0437 "	57.434
3.	4.9601 "	2.8497 "	57.449
	Mean value		57.442

Second Series of Analyses.

Wt. taken. Argentic bromide.	Wt. taken. Argentic chloride.	Wt. taken. Silver.	Wt. calculated. Silver.
0.9389 gram.	1.0498 gram.	1.3283 gram.	1.3293 gr.
1.0915 "	1.3042 "	1.6095 "	1.6086 "
1.1779 "	1.2551 "	1.6229 "	1.6217 "
1.2470 "	1.5420 "	1.8778 "	1.8770 "
1.6153 "	0.6661 "	0.8560 "	0.8550 "

The slight increase of variation between the found and calculated results in this second series of analyses I attribute to a slight volatilization of the argentic chloride before the bromide undergoes fusion.

With the argentic iodide I have only tried qualitative experiments, but I can see no reason why its determination when mixed with either argentic chloride or bromide cannot be accomplished according to this method.

XVI.—THE DECOMPOSITION OF PHENYLTRIBROMPROPIONIC ACID BY WATER.

By Leonard J innicutt.

Glaser in his study of the addition products of cinnamic acid obtained two isomeric phenyltribrompropionic acids, and observed that they were decomposed by boiling water.[1] The nature or constitution of the substances was not investigated. In the hope that one of the products of this decomposition might be a phenylmonobromglyceric acid, the result of a reaction analogous to the formation of phenylmonobromlactic from phenylbibrompropionic acid, I undertook a study of these substances, and, although the work is not as yet completed, I have thought best to publish the few results so far obtained.

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[1] Annalen der Chemie, **143**, 335 and 339.

The two phenyltribrompropionic acids were obtained by Glaser by the action of bromine on the α- and β-monobromcinnamic acids, these two acids being formed by the action of alcoholic potash on phenylbibrompropionic acid.[1] In repeating this work I could not obtain a satisfactory yield of the monobromcinnamic acids; if, however, the ethyl ether, which is formed by the action of bromine on the ethyl ether of cinnamic acid,[2] is taken, the amount obtained averages nearly ninety per cent. of the theoretical.

The separation of the two monobrom-acids was effected by Glaser, by taking advantage of the differences in the solubility of their ammonium salts.[3] This seems to me unnecessary, as the α-acid itself is much less soluble in boiling water than the β-acid. Bromine, I found, would not act on the α-acid in a solution of bisulphide of carbon, and the tribrom-product was obtained by the action of bromine on the dry acid.[4] The substance formed is easily purified by recrystallization from bisulphide of carbon. It melts at 132° with slight decomposition.

Eight grams of this acid were placed in a flask with one hundred cubic centimeters of boiling water, and steam passed through the liquid; an oil was carried over, and the clear liquid on cooling deposited a crystalline substance, which had all the properties of α-monobromcinnamic acid, melting at 132.6°, soluble in boiling water, from which it crystallized on cooling.

A bromine determination gave the following results:

$$C_6H_5.CH=CBr.COOH.$$

Taken.	Found.	Calculated.
0.2300 gram	0.2216 gram AgBr.	
	35.37 per cent. Br.	35.25 per cent. Br.

The oil that was carried over by the steam was separated from the water by filtration, and after thorough washing to remove all the hydrobromic acid, was dried over sulphuric acid. Two determinations gave the following amounts of bromine:

Taken.	Found.
0.2332 gram	0.3370 gram AgBr = 61.48 per cent. Br.
0.2220 "	0.3213 " AgBr 61.52 " Br.

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[1] Ibid. **143**, 332.

[2] Berichte der deutschen chemischen Gesellschaft, **11**, 1219.

[3] Annalen der Chemie, **143**, 332.

[4] Ibid. **143**, 335.

This oil is evidently a bibromstyrene, the percentage of bromine required for that substance being 61.30. It is of a light yellow color, with an odor resembling bromstyrene. On being heated, hydrobromic acid is given off, and at a temperature of about 253° an oil begins to distill over. This oil was evidently a mixture, for on analysis it gave 59.35 per cent. bromine.

The decomposition of α-phenyltribrompropionic acid by water consists therefore in the splitting off both of bromine and hydrobromic acid, with the formation of α-monobromcinnamic acid and a bibromstyrene. The action of water on the β-tribrom-acid is without doubt analogous. This, together with a further study of the two tribrom-acids, and of the new bibromstyrene, I have already undertaken.

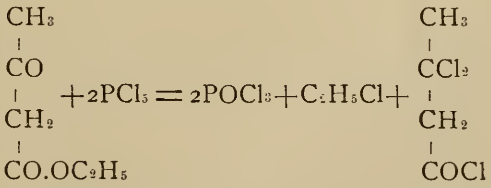
ON THE PROPYL DERIVATIVES AND DECOMPOSITION PRODUCTS OF ETHYL ACETOACETATE.

By Beverly S. Burton.

(Continued from Vol. 3, p. 395.)

Action of Phosphorus Pentachloride upon Diethyl Acetoacetate.

The action of phosphorus pentachloride upon ethyl acetoacetate was first studied by Geuther and Froehlich,[1] who obtained two isomeric chlorcrotonic acids. In all probability, the first phase of the reaction is the formation of the chloride of betadichlorbutyric acid, thus:



$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{CO.OC_2H_5} \end{array} + \mathrm{2PCl_5} = \mathrm{2POCl_3} + \mathrm{C_2H_5Cl} + \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CCl_2} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{COCl} \end{array}$$

This then loses hydrochloric acid, the hydrogen being taken, partly from the alpha-position and partly from the end methyl group, and there are formed, simultaneously, the chlorides of the two isomeric chlorcrotonic acids:

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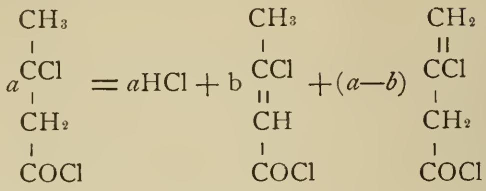
[1] Zeitschrift für Chemie, 1869, 270.

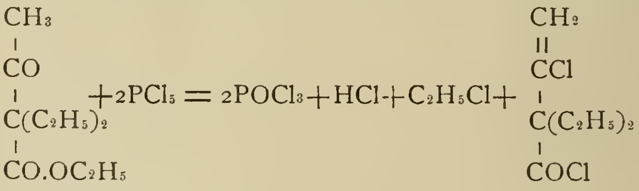


$$a\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{CCl}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{COCl}\end{array} = a\mathrm{HCl} + \mathrm{b}\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{CCl}\\ \|\\ \mathrm{CH}\\ |\\ \mathrm{COCl}\end{array} + (a-b)\begin{array}{c}\mathrm{CH_2}\\ \|\\ \mathrm{CCl}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{COCl}\end{array}$$

The liquid product gives the corresponding acids when treated with water, and these can be readily separated from each other by taking advantage of differences in their volatility and solubility. The chlorine atom in the two acids thus obtained can be readily replaced by hydrogen when treated with sodium amalgam.

Rücker[1] attempted later, by the action of phosphorus pentachloride upon methyl ethylacetoacetate, to obtain the corresponding isomeric methylcrotonic acids. There was, however, only a single methylchlorcrotonic acid obtained, which by the action of sodium amalgam could not be converted into methylcrotonic acid. It is then shown by these experiments of Rücker that there is a very marked and decided difference in the action of phosphorus pentachloride upon ethyl acetoacetate, and upon its methyl substitution product.

In view of these differences it was of special interest to further study the action of phosphorus chloride upon the dialkyl derivative of ethyl acetoacetate. It was to be expected that by the action of phosphorus chloride upon diethyl ethylacetoacetate the chloride of chlordiethylisocrotonic acid would be formed, thus:



$$\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{C(C_2H_5)_2}\\ |\\ \mathrm{CO.OC_2H_5}\end{array} + 2\mathrm{PCl_5} = 2\mathrm{POCl_3} + \mathrm{HCl} + \mathrm{C_2H_5Cl} + \begin{array}{c}\mathrm{CH_2}\\ \|\\ \mathrm{CCl}\\ |\\ \mathrm{C(C_2H_5)_2}\\ |\\ \mathrm{COCl}\end{array}$$

The reaction does not, however, take place as here expressed, but the molecule is split up, as the following investigation shows.

The diethyl ethylacetoacetate was prepared according to the modified process of Conrad and Limpach, and that portion boiling between 210° and 215° was employed. In a flask connected with an inverted condenser were brought 65 grams (2½ mol.) of phosphorus chloride, and 20 grams of the ether were gradually added. Before heating, the action was very slight, but by gentle warming on the water-bath a very regular evolution of gas took place, which became violent when the temperature was increased to the boiling of water. The heating was continued for two days. When the reaction was complete, the product was poured into cold water; a heavy liquid separated and sank to the bottom. This was washed and dried over sulphuric acid. A portion was subjected to distillation. At 150° decomposition ensued, the liquid becoming dark and evolving acid fumes, but as the distillation in a current of steam could be effected, this method was employed. The product was separated from water and dried as before. This product is a colorless liquid, which by keeping turns slightly yellow and becomes acid. Concentrated solutions of alkaline carbonate and hydrate, even on boiling, had no noticeable effect upon it, clearly showing that the expected acid was not formed.

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[1] Annalen der Chemie, **201**, 34.

In the course of the experiments to be described later, it was found necessary to prepare a second portion of this product, which was carried out with every possible precaution and care. Repeatedly fractionated diethyl ethylacetoacetate, boiling between 210° and 212°, a combustion of which gave results agreeing closely with the theory, was treated as before with phosphorus pentachloride. The product was treated with sodium hydrate, thoroughly washed with water, dried over sulphuric acid, and then kept in contact with ignited potassium carbonate, the portions filtered off and employed for analysis were perfectly neutral to test-paper.

Under Nos. I. and II. are the results from the combustion of the product obtained by the first preparation.

Under III., IV., V., VI., VII., those from the second.

The results of the analyses in which lead chromate and a silver spiral were laid before the copper oxide are the following:

I. 0.2062 gram substance yielded 0.1333 gram H_2O and 0.3906 gram CO_2
II. 0.2054 " " " 0.1350 " H_2O " 0.3885 " CO_2
III. 0.2694 " " " 0.1804 " H_2O " 0.5113 " CO_2
IV. 0.2460 " " " 0.1648 " H_2O " 0.4675 " CO_2

Chlorine Determinations.

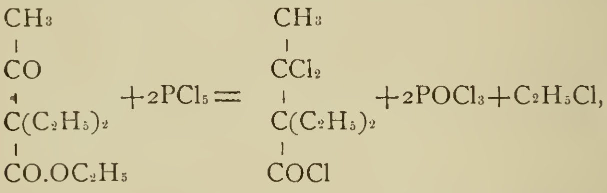
V.	0.4693	gram	substance	yielded	0.4125	gram	AgCl
VI.	0.4518	"	"	"	0.3954	"	AgCl
VII.	0.4571	"	"	"	0.3983	"	AgCl

From the above is calculated the formula $C_7H_{11}ClO_2$.

	Calculated.	I.	II.	III.	IV.	V.	VI.	VII.
C_7	51.69	51.71	51.58	51.76	51.79	..	..	..
H_{11}	6.77	7.19	7.30	7.44	7.44	..	..	..
Cl	21.85	..	..	..	..	21.74	21.65	21.56
O_2	19.69	..	..	..	..	..	..	..
	100.00							

The chlorine was determined according to Carius's method. In order to effect a complete decomposition, it was found necessary to employ fuming nitric acid, and to maintain a temperature of 160° for several hours.

The anticipated dichlor substitution-product is not formed in the normal manner as expressed in the equation,



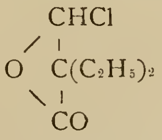
$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ C(C_2H_5)_2 \\ | \\ CO.OC_2H_5 \end{array} + 2PCl_5 = \begin{array}{l} CH_3 \\ | \\ CCl_2 \\ | \\ C(C_2H_5)_2 \\ | \\ COCl \end{array} + 2POCl_3 + C_2H_5Cl,$$

but decomposition ensues, one product of which is an oil containing chlorine. At the same time a gas is evolved, in all probability methyl chloride.

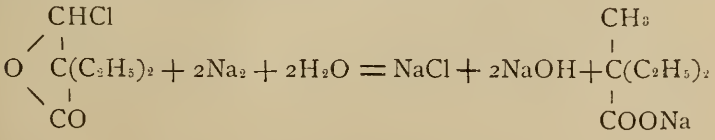
In order to study more closely the nature of this reaction, and to determine, if possible, the nature of the gaseous product, the above described process was repeated with the following modification: 67.2 grams (2 molecules) of phosphorus pentachloride were introduced into a flask connected with an inverted condenser, and the apparatus filled with carbon dioxide. There were now gradually added 30 grams of ether by means of a dropping funnel, and the evolved gases collected in a mercury gasometer, which contained a layer of strong caustic potash. In the course of several hours 200 cc. of gas were collected, this was dried by passing over calcium chloride, then conducted through two U-tubes, the first standing in a freezing mixture of ice and salt, the second in one of ice and crystallized calcium chloride which showed a temperature of —37°. As soon as the gas was driven out of the gasometer, the two tubes still in the freezing mixture were sealed by means of a blowpipe. In both were condensed a small quantity of liquid; that in the second tube disappeared when removed from the freezing mixture, but reappeared when again immersed. On opening the tube the gas, which violently escaped, burned with a green coloration of the flame, from which it may be concluded, with considerable probability, that this was methyl chloride. The first tube did not show these characteristics in so marked a manner, and was, apparently, ethyl chloride formed as indicated in the above equation. The splitting off of the methyl group is of special interest, as it is the first time that this phase of the decomposition of the ethyl acetoacetate molecule has been observed.

Action of Sodium Amalgam upon the Oily Product $C_7H_{11}ClO_2$.

It is difficult as yet to make any definite statement as to the constitution of the remarkable oily product corresponding to the empirical formula $C_7H_{11}ClO_2$. It possesses no acid properties, since it is not changed by caustic alkalies. It is rather to be regarded as a body with marked lactone characteristics, and possessed of great stability toward alkaline hydrates. That one of the oxygen atoms is present as carbonyl (CO) appears probable, and that the position of the two ethyl groups has not been changed, the chlorine atom being, without doubt, united with the ketone carbon atom of the diethyl acetoacetate. Assuming then the lactone character of the body, its constitution could be expressed by the formula.



It was now considered interesting to effect if possible the replacement of the chlorine atom by hydrogen by means of sodium amalgam, the further action of the sodium hydrate formed in the reaction giving rise, possibly, to a crystallizable salt of methyldiethyl acetic acid in the following manner:



The product was mixed with alcohol, and water added until quite turbid. Then four per cent. sodium amalgam was introduced. The reaction took place slowly, and the volume of the oil decreased until it entirely disappeared in the resulting alkaline liquid. This was then neutralized with sulphuric acid, and repeatedly extracted with ether, separated, and the ether distilled off. The residue was again treated with sodium amalgam, neutralized, and extracted with ether as before, until all the oil was thoroughly decomposed. The neutralized solutions were then evaporated to dryness, and repeatedly extracted and purified with absolute alcohol.

The filtered alcoholic solutions left, on evaporation, an extremely deliquescent sodium salt, which, however, still contained a very little chlorine. A small portion acidified with sulphuric acid deposited oily drops, which possessed the characteristic odor of the higher fatty acids.

An attempt was made to remove the chlorine present by partial precipitation with silver nitrate, which was continued until the formed precipitate dissolved clear in nitric acid, then all was precipitated with silver nitrate. The separated organic silver salt formed a white powder, not readily affected by light, which could be dried without decomposition. The analysis yielded the following results:

I. 0.2368 gram silver salt yielded 0.2712 gram CO_2, 0.0975 gram H_2O, and 0.1156 gram residue.

II. 0.2098 gram silver salt yielded 0.2400 gram CO_2, 0.0861 gram H_2O, and 0.1027 gram residue.

The percentage composition calculated from the above is:

	I.	II.
C	31.24	31.21
H	4.58	4.56
Residue	48.82	48.95

An examination of the residue showed that 0.1156 gram of the same contained 0.0300 gram of silver chloride.

By protracted boiling of the silver salt with a large amount of water and allowing to cool, various portions of crystallized salt were obtained. Two different portions yielded the following results:

I. 0.1943 gram silver salt yielded 0.2352 gram CO_2, 0.0841 gram H_2O, and 0.0936 gram residue. 0.0616 gram residue contained 0.0320 gram silver chloride=4.37 per cent. Cl.

II. 0.1912 gram silver salt yielded 0.2233 gram CO_2, 0.0799 gram H_2O, and 0.0919 gram residue. 0.0583 gram residue contained 0.0336 gram silver chloride=4.35 per cent. Cl.

Expressed in percentages:

	I.	II.
C	33.01	31.85
H	4.81	4.64
Residue	48.17	48.07

The composition had thus not materially changed, and no formula could be calculated. A determination of the chlorine was then made by Carius's method.

0.3942 gram of the silver salt gave, by complete oxidation with fuming nitric acid in a sealed tube, 0.0670 gram silver chloride, corresponding to 4.20 per cent. chlorine. This chlorine residue is due, undoubtedly, to the presence of an organic acid containing chlorine.

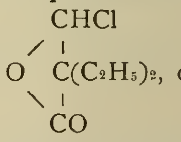
An experiment showed that the acid mixture separated by a mineral acid could be distilled without decomposition, and this method was now resorted to for its purification. The sodium salt was decomposed with very dilute sulphuric acid, the oily layer separated, and the aqueous solution extracted with ether. The acid so obtained was then subjected to fractional distillation. The boiling point rose very rapidly to 185°; by far the greater portion distilling over at 190°–192°, leaving a residue which on heating evolved fumes of hydrochloric acid. After repeated distillation the fraction 190°—192° showed on ignition with sodium only traces of chlorine. A combustion was then made yielding the following results:

I. 0.1832 gram of acid gave 0.4127 gram CO_2, and 0.1759 gram H_2O.

II. 0.1922 gram of acid gave 0.4355 gram CO_2, and 0.1796 gram H_2O.

From this is calculated the formula of diethylacetic acid, with which this acid fully agrees in boiling point and all other properties.

	Calculated.	Found. I.	Found. II.
C_6	62.07	61.44	61.80
H_{12}	10.34	10.67	10.38
O_2	27.59	...	...
	100.00	...	...

By far the larger portion of the oil $C_7H_{11}ClO_2$ is then, by treatment with sodium amalgam, converted into diethylacetic acid. What is formed here at the same time as a by-product in the reaction I have not been able as yet definitely to determine. The fact, however, of the splitting off of a carbon atom is established, completing and confirming the observations previously made as to the slight binding power or affinity of the carbon atom, combined with the two alkyl groups, and the carbon atom of the ketone group in the diethyl acetoacetates. By saponification with alkalies, diethyl acetoacetate splits up into diethylacetic acid and acetic acid. By heating diethyl betaoxybutyric acid splits up into diethylacetic acid and aldehyde, as does also dipropyl acetoacetate by the mere attempt to convert it into the corresponding oxyacid, and so, finally, phosphorus pentachloride splits up the molecule of diethyl acetoacetate, though not at the same point, the first phase in the reaction being the removal of the methyl group which escapes as methyl chloride, giving rise to a compound which, in contact with water, is converted into the body  $\mathrm{O}\left\langle\begin{array}{l}\mathrm{CHCl}\\ \mathrm{C(C_2H_5)_2}\\ \mathrm{CO}\end{array}\right.$, of the nature of an anhydride such as lactone; and this by further treatment with sodium amalgam suffers the normal decomposition of the dialkyl acetoacetate already mentioned, giving rise to diethyl acetic acid.

I desire to express here my thanks to Professor Wislicenus, in whose laboratory these investigations were carried out, for his uniform kindness and many valuable suggestions.

Contributions from the Sheffield Laboratory of Yale College.

XI.—ON UREA FROM AMMONIA AND CARBON DIOXIDE.

By W. G. Mixter.

The well-known formation of urea when ammonium carbamate is heated in sealed tubes to 140°C. suggested the possibility of making urea by passing ammonia and carbon dioxide through a warm tube. It was found, however, that the two gases do not react on each other at temperatures somewhat below a visible red, but that at a red heat products are formed which yield urea beautifully crystallized in the cooler parts of the tube, where the heat nevertheless is sufficient to prevent the condensation of ammonium carbamate and carbonates. The urea forms very slowly, and the yield is apparently not increased by heating a greater length of tube, or by passing the gases over charcoal or platinized asbestos. The greater part of the ammonia and carbon dioxide passes unchanged, and more water is formed than corresponds to the urea produced. The substance used for analysis was made as follows: Dry ammonia and carbon dioxide were passed separately into the hot part of a combustion tube, which was heated to redness in a combustion furnace by four or five burners. A second portion of the tube eight or nine inches from the first hot part was also heated. To facilitate condensation, the tube, which was about two centimeters wide, was enlarged to bulbs of four or five centimeters in the parts anterior to the heated places. The bulbs were protected from the intense heat by screens, and were usually hot enough to prevent the deposition of ammonium salts. If these condensed with the urea, they were driven off by careful heating. The urea formed at the rate of a decigram to decigram and a half an hour. A slight opaque white sublimate formed between the urea and the hot part of the tube. The urea was dissolved in absolute alcohol, the solution was evaporated and the residue was dried at 100°C., and finally in a vacuum over oil of vitriol. It melted at 131°C.[1]

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[1] Lubavin, Berichte der deutschen chem. Gesell. 3, 303, found the melting point of urea from potassium cyanate to be 132°C.

The nitrogen was determined by a combustion with soda-lime and titration.

	Urea.	Found.	
C	20.	20.50	20.29
H	6.66	6.86	6.79
N	46.67	46.14	
O	26.67		

The excess of carbon and the deficiency of nitrogen found is doubtless due to the loss of some ammonia during the long exposure to heat in making. A titration with mercuric nitrate solution gave 99.02 per cent. of urea. The identity of the substance with urea was further confirmed by the following properties: It gave off ammonia when heated, and the residue gave the biuret reaction with copper sulphate and caustic potash. It did not react for biuret or cyanuric acid before heating. The nitrate separated on adding nitric acid to the aqueous solution in apparently the characteristic form of urea nitrate.

It is evident that urea is not the direct product of the reaction between carbon dioxide and ammonia, as it is decomposed at the temperature used in the experiment.

The formation of urea in the way described is undoubtedly preceded by the formation of other bodies, and probably by the production of cyanic acid, thus:

$$CO_2+NH_3=HCNO+H_2O.$$

If cyanic acid is formed it would unite with ammonia in the cooler part of the tube to form urea, as was proved by passing cyanic acid, prepared from cyanuric acid, and ammonia through a red-hot tube. The reaction here suggested as probable is analogous to that which, according to Kuhlmann, occurs when ammonia and carbon monoxide are passed over heated platinum sponge in a tube,[1] the final product of which may be represented thus:

$$CO+2NH_3=NH_4CN+H_2O.$$

But since ammonium cyanide cannot exist at a high temperature, hydrocyanic acid is doubtless first formed and combines with ammonia in a cooler part of the apparatus,

$$(NH_3+CO=HCN+H_2O \text{ and } HCN+NH_3=NH_4CN).$$

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[1] Graham-Otto **1**, 1127.

Further evidence that the production of cyanic acid precedes the formation of urea was found in the fact that alkali cyanates are formed when ammonia and carbon dioxide pass over hot alkali carbonates.

Herroun[1] obtained urea by passing air, ammonia and benzene vapor over a hot coil of platinum. In view of the results of the above described experiment, it seems reasonable to suppose that the urea which Herroun obtained resulted also from the action of carbon dioxide on ammonia, since benzene with an excess of air would produce carbon dioxide.

On Cyanates from Ammonia and Carbon Dioxide.

If the assumption is correct that the formation of urea in the foregoing experiment is preceded by the formation of cyanic acid, the production of cyanates might be expected if some substance capable of combining with that body were present. The result of the following experiments shows that cyanates are actually formed under such conditions. A preliminary trial was made by passing cyanic acid from cyanuric acid over red-hot magnesia, lime and sodium carbonate. The first two did not take up cyanic acid, while the latter was partially converted into sodium cyanate. Dry carbon dioxide and pure dry ammonia were passed through a combustion tube containing sodium carbonate heated to redness, but not hot enough to fuse the pure carbonate. The mass in the tube began to soften at the end where the gases first came in contact with it. As soon as one part was fused the heat was lowered somewhat to prevent danger from overheating and partial decomposition of the cyanate formed. In an hour the experiment was ended, and the flow of the ammonia was then stopped, and the current of the carbon dioxide was continued a few minutes to expel the ammonia. The saline mass gave off ammonia very slowly on boiling with water, but after saturating with hydrochloric acid and adding an excess of caustic potash, ammonia was freely evolved. 3.4 per cent. of nitrogen[2] were found in a portion where the gases first came in contact with the sodium carbonate, and 1.1

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[1] J. Chem. Soc. Oct. 1881, 471.

[2] The method used in estimating nitrogen is based on the formation of ammonium salts when cyanates are treated with an acid. Two test determinations of the nitrogen in pure potassium cyanate were made by dissolving the salt in dilute hydrochloric acid, then adding potash and distilling into standard acid and titrating; 16.06 and 16.07 per cent. of nitrogen were found; theory requires 17.02 per cent. Whether the loss was due entirely to the setting free of some cyanic acid, by the action of the acid on the cyanate, was not determined. All the nitrogen estimations were made by this method.

per cent. in a part near the open end of the combustion tube. Potassium carbonate behaves like sodium carbonate and yields a product more fusible than potassium carbonate. In one experiment a portion from near the posterior end of the tube in which the carbonate was heated yielded 4.3 per cent. of nitrogen, corresponding to 25 per cent. of potassium cyanate. This product from the potassium carbonate gave the odor of cyanic acid when dissolved in dilute hydrochloric acid. Another part of the same product was dissolved in water, ammonium sulphate was added and the whole was evaporated, the residue was exhausted with alcohol, and from the alcoholic solution urea was obtained.

It must be admitted that the production of cyanates by this method does not positively prove the previous formation of cyanic acid, since some cyanate is formed by the reaction of ammonia alone on sodium carbonate. In one experiment dry ammonia was passed over sodium carbonate which was gradually heated to fusion, and 1.2 per cent. of nitrogen was found in the product. A similar experiment in which potassium carbonate was used yielded 1.1 per cent. of nitrogen. These amounts of nitrogen, which were the highest obtained in several such experiments, show that from one-quarter to one-third as much cyanate was formed as when carbon dioxide was used.

It should be mentioned that, in making cyanates from alkali carbonates, ammonia and carbon dioxide, no cyanides were formed when pure ammonia[1] was used, but that when ammonia gas from a good quality of commercial ammonia water was used, the solution of the saline mass reacted distinctly for cyanides with ferrosoferric sulphate and an acid.

When soda-lime is exposed to the combined action of carbon dioxide and ammonia, only that portion next the posterior end of the heated tube yields ammonia, and only traces of it. Dr. E. H. Jenkins informed the writer that he obtained no ammonia on boiling the soda-lime after making a combustion of dried blood.

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[1] The pure ammonia was prepared from sal ammoniac which was freed by Stas's method from compound ammonias by boiling a saturated solution with nitric acid. The ammonia was liberated by lime and dried by caustic potash.

ACONITIC ACID IN THE SCALE FROM SORGHUM SUGAR PANS.

By Henry B. Parsons.

Clear, defecated sorghum juice, after treatment with milk of lime to faint alkalinity, slowly deposits, on further boiling, a light buff-colored scale, which adheres tenaciously to the evaporating pan, and, being a poor conductor, causes a considerable loss of available heat.

This scale is easily soluble, without effervescence, in hydrochloric acid, the resulting solution giving abundant evidence of lime and magnesia, but no tests for sulphate, glucose, or sucrose; hence the scale is neither calcium sulphate nor any compound of lime with sucrose, as was at first surmised.

A careful analysis of an air-dry sample resulted as follows:

Analysis of Scale from Sorghum-Sugar Pans.

Moisture, loss at 125° C.	7.48
Silica and clay, insoluble in HCl	1.57
Oxides of iron, aluminium, and manganese,	.57
Phosphoric anhydride (P_2O_5)	.19
Calcium oxide, (CaO)	22.87
Magnesium oxide, (MgO)	3.65
Alkalies,	traces
Organic matter, by difference,	63.67
	100.00

As lime was originally used in excess, the magnesia present was believed to be in the form of oxide, uncombined with the organic matter at least, though a portion may have been combined as phosphate. Rejecting accidental impurities and considering this scale as an impure lime salt, we have:

	Obtained.	In 100 Parts.
Water, H_2O,	7.48	7.95
Calcium oxide, CaO,	22.87	24.32
Organic,	63.67	67.73
	94.02	100.00

Upon dividing the figures in the second column by the molecular weights, respectively, of water, calcium oxide, and the calculated molecular weight of the organic matter, we obtain results which leave little room for doubt that this substance is a simple, definite salt of calcium: thus:

Water, H_2O, $7.95 \div 18 = .4417 = 1$
Calcium oxide, CaO, $24.32 \div 56 = .4343 = 1$
Organic, $67.73 \div 155.3 = .4361 = 1$

A small portion of what proved to be the organic acid was separated in nearly pure condition, by boiling the finely pulverized scale with an amount of dilute sulphuric acid not sufficient to combine with all the lime and magnesia present.

The clear, golden-yellow filtrate had a strong acid reaction not due to sulphuric acid, and contained considerable magnesium sulphate, a little calcium sulphate, and a small amount of manganese as soluble salt. Upon treating this solution with twice its volume of absolute alcohol the calcium and magnesium sulphates were precipated. The filtrate, evaporated to a small bulk, was treated with excess of absolute alcohol, whereby a magnesium salt of the organic acid was precipitated.

This salt (A) was well washed with absolute alcohol, then with ether, dried and pulverized; it was nearly white. Upon gentle ignition a pink residue remained, which became dark brown upon further heating. As this salt (A) was perfectly soluble in water, and as inorganic acids were proved to be absent, it appears that manganous oxide must have partially replaced the magnesium oxide in this salt. The following is the analysis:

Composition of Magnesium Salt. (A).

	Air Dry.	Dried at 125° C.
Water, H_2O,	9.97	...
Manganous oxide, MnO,	.98	1.09
Calcium oxide, CaO,	5.20	5.78
Magnesium oxide, MgO,	14.05	15.60
Organic, by difference,	69.80	77.53
	100.00	100.00

Calculating the manganous and calcium oxides to their magnesium oxide equivalents, we have for the dry salt:

Magnesium oxide, MgO, $20.35 \div 40.0 = .5088 = 1$
Organic, $79.65 \div 156.6 = .5086 = 1$

An aqueous solution of this salt gave the following reactions:

Silver Nitrate: A scanty white precipitate, dissolved and blackened by boiling.

Lead Acetate: A bulky white precipitate.

Mercuric Chloride: A moderate amount of yellowish-white precipitate.

Mercuric Nitrate: A bulky white precipitate.

Copper Sulphate: A bulky white precipitate.

Ferric Chloride: Concentrated solution, a bulky gelatinous, yellowish-red precipitate.

Barium Chloride: No precipitate.

These reactions led to the belief that the acid must be *aconitic*, and further study and analytical results confirm this opinion.

The filtrate from salt (A) was concentrated until free from alcohol, and after cooling, treated with excess of stronger ether, whereby a yellowish, stringy, hygroscopic mass was precipitated; this proved to be a mixture of salt (A) with free organic acid. It was freely soluble in water, partially in alcohol. It was not further examined.

The ethereal filtrate from this treatment had a lemon-yellow color, a strong acid reaction, and when heated, gave off acid vapors, took fire readily, and left an unweighable ash. A second solution in ether and filtration furnished the ash-free acid, which slowly crystallized in imperfect warty masses. From this acid the zinc, lead, and silver salts were prepared as follows:

1. *Zinc Salt.*—A dilute aqueous solution of the acid was heated for several hours on the water-bath with excess of pure zinc oxide. The filtrate was evaporated and dried at 110° C. to a constant weight. Continuous ignition, with use of nitric acid, left a residue of zinc oxide equal to 34.15 per cent. of the dry salt.

2. *Lead Salt.*—A slightly alkaline (ammoniacal) solution of the acid was made faintly acid with acetic acid and precipitated by normal lead acetate. The white precipitate was washed with water in a Gooch crucible, dried *in vacuo*, and to a constant weight at 100° C., and carefully ignited; 69.18 per cent. of lead oxide was thus obtained.

3. *Silver Salt.*—A cold, neutral ammonium salt of the acid was precipitated by the solution of silver nitrate, the white precipitate well washed, dried at 110° C., and ignited. This salt was slightly blackened and decomposed about the edges before ignition; 64.42 per cent. of silver was found.

Owing to lack of material no further determinations were made, yet it is believed that the following results taken in connection with the exact correspondence in qualitative reactions, will justify the assertion that this sorghum-sugar scale is a two-thirds metallic calcic aconitate containing one molecule of combined water ($CaHC_6H_3O_6.H_2O$).

	Formula.	Sought.	Found.	Theory.
Calcium salt,	$CaHC_6H_3O_6.H_2O$,	CaO,	24.32	24.35
		H_2O,	7.95	7.82
Magnesium salt,	$MgHC_6H_3O_6$,	MgO,	20.35	20.41
Zinc salt,	$ZnHC_6H_3O_6$,	ZnO,	34.15	34.22
Lead salt,	$Pb_3(C_6H_3O_6)_2$,	PbO,	69.18	69.42
Silver salt,	$Ag_3C_6H_3O_6$,	Ag,	64.42	65.38

The presence of aconitic acid in meladoes from the West Indies was proved by A. Behr;[1] the presence of the same acid in the juice of sorghum, a plant somewhat closely related to sugar cane, is interesting in that it is another instance of the many similarities in chemical composition which have been noted of late years, in plants of the same or closely allied families and orders.

I am indebted to Mr. Clifford Richardson, of the Department of Agriculture, Washington, D. C., for the completion of work upon the lead, silver, and zinc salts.

New York, Jan. 1882.

APPARATUS FOR THE ABSOLUTE DETERMINATION OF NITROGEN.

By Thomas S. Gladding.

The great value of the azotometer and mercury pump, devised by Professors S. W. Johnson and E. H. Jenkins,[1] and their rapidly extending use, will make any worthy improvement thereon welcome.

In the accompanying cut, improvement has been sought on four points.

1st. In a more rapid exhaustion of the combustion tube.

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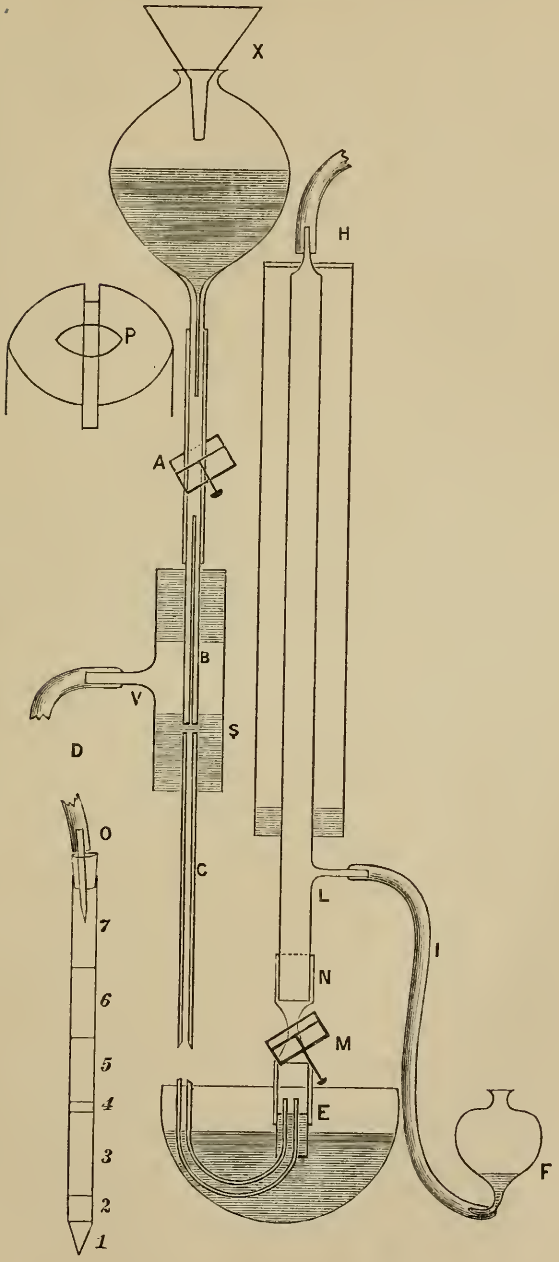
[1] Berichte der deutschen chemischen Gesellschaft, **10**, 351.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2d. In a simpler and easier method of collecting the nitrogen gas.

3d. In the attainment of a constant suction on the combustion tube, thereby preventing blowing-out of the tube, so frequently a source of trouble to the analyst; and

4th. In the more thorough preliminary exhaustion of the combustion tube and the consequent greater accuracy of the analysis.

A few words only will be needed to explain the accompanying section of the apparatus. Upon the side of the glass tube S is blown a stout piece of glass tubing V. The pure (so called) rubber tubing D, with walls 4 mm. thick to prevent collapse from atmospheric pressure, serves to connect the pump with the combustion tube, and is securely bound to the tubes V and O (which are previously smeared with glycerine) by means of copper wire wound as tightly as possible. This tube D is clamped securely to the wooden frame of the apparatus just beyond the glass tube V, in order to remove the latter from all strain. The barometer tubing C, 7 mm. in diameter, is forced up to within 5 mm. of the top of the rubber cork S. The tube B is forced through the cork B into the cork S to within 1 mm. of the tube C. The bore of B is about one-half that of C and is held exactly over the latter. The flow of mercury is regulated by the clamp A. The rubber tube A is bound tightly to B, its walls are 2 mm. thick, and it is wrapped with one layer of kid or chamois skin to prevent wear by the action of the clamp A. The tube C is about 45 inches in length and curves up into the glass tube E. A stout glass finger-bowl is admirably adapted to serve as the vessel E. The tube E is connected with N by a large rubber tube tightly bound to both and closed at pleasure by the large screw clamp M. The cork S is shown in nearly top section at P. A slot about 3 mm. wide and 5 mm. deep is cut straight across the cork. In this way free access of the gas to be pumped off is given into the tube C, and at the same time the tube B is held exactly over the former.

The first point of improvement, viz. the more rapid exhaustion of the air in the combustion tube, is obtained by the peculiar construction of the pump. The tube B delivers exactly into C, and the bore of C being larger than that of B, there is no choking. The bore of C may be as large as 2 mm. With such a size a complete

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[1] This Journal, 2, 27.

vacuum in the combustion tube is easily obtained in from four to five minutes.

The second point of improvement is understood from the figure. The curving of the tube C up into E for the distance of 1½ inches removes all danger of loss of nitrogen and all necessity of handling or moving about any part of the apparatus.

The third point is obtained by the method of collecting the gas. When M is open and the reservoir F is placed a few inches below the level of the mercury in the vessel E, the pressure upon the mercury in the tube E is diminished, the mercury rises slightly in the tube E, and the internal pressure upon the walls of the combustion tube is correspondingly diminished. Provided no stoppage takes place in the tube itself from too close packing or the use of too fine a filling, no tube can blow out if this device is used. This suction may be increased at pleasure by lowering the vessel F still more, but a gentle aspiration is usually sufficient and safer.

The fourth point, a more thorough exhaustion of the gas in the combustion tube, is effected as follows: About 0.6 gram of bicarbonate of soda is placed in the tail of the tube at 1. The use of chlorate of potash has been found unnecessary in all ordinary work, from duplicate analyses performed with and without it. Its use introduces, moreover, a possible escape of oxygen gas beyond the metallic copper and a consequent error in the analysis. The space 2, about two inches in length, is filled with ignited asbestus. This is followed by the substance to be analyzed at 3, mixed with copper oxide. This latter is about as fine as sea-sand, and is freed from dust or pulverized copper oxide by means of a fine sieve. It is strongly ignited and mixed with the substance while still warm. At space 4 is another 0.6 gram of bicarbonate of soda. This is followed by a layer of copper shot at 5, and this again by a layer of coarsely granulated copper oxide. The analysis is begun by drawing the potash solution nearly to the top of the azotometer, then turning up lamps under 6 and at the same time starting the pump. When a perfect vacuum has been obtained and the copper oxide 6 is red hot, the lamp just beyond 1 is turned up, and a gentle heat just sufficient to drive off the CO_2 from it and not to heat space 3 is applied. When the tube is full of CO_2 this lamp is turned off and the tube again exhausted. By this process of washing out the tube, several tenths of a cc. of additional gas are obtained, and almost the last traces of air are removed. The object in using finely granulated copper oxide free from the powder is to give full play to this washing. On running the heat back the bicarbonate at 4 gives off CO_2 and refills the tube before the combustion of the substance at 3 begins. At this stage, draw the potash solution again up to H.

To fill the azotometer with the potash solution, pinch the rubber tube I, and by the suction of the mouth applied at the rubber tube H draw the mercury up as far as the tube L. Holding it there, close the clamp M, raise the reservoir F and fill it with the potash, which rises of course in the azotometer LH.

While the apparatus is in this condition, the tube remaining filled with mercury from M to L, the azotometer may be lifted and removed from the pump for any repairs without mixing the mercury and potash solution. In this position also it may be washed out for a fresh filling. Lower the reservoir F and invert it into a beaker. Upon opening the cock H all the potash runs out, and the tube HL may be rinsed clean with dilute acid introduced at H. The potash in tube LH may be drawn up to the glass cock H, either by closing the clamp M and then raising F to the level of H. or by the suction of the mouth applied at the rubber tube H. When the apparatus is not in use, F should be on a level with E to prevent any possible aspiration of air into the azotometer tube from the tube C.

Two simple rules may be given to prevent the potash solution in N from ever escaping into the vessel E: Close clamp M (1) whenever F is to be raised above E; (2) whenever the glass cock H is to be opened.

Lab. of Stillwell & Gladding, New York.

THE ESTIMATION OF UREA BY SODIUM HYPOBROMITE.

By J. R. Duggan.

Since Knop, in 1854, announced his method for the estimation of urea by the amount of nitrogen evolved on the addition of an alkaline hypobromite, there has been considerable discussion concerning its accuracy. The method requires so little time and skill in its application, that this question is the only one necessary to decide its precedence over all others. Although a few observers have obtained nearly perfect results in its use, it is generally admitted that only about 92 per cent. of the whole amount of nitrogen is liberated by the hypobromite; and this error is not very constant. For clinical purposes even this approximation is of value, but in physiological investigations greater accuracy is required.

Some time ago I began work on this method to find what conditions were necessary to give the best and most uniform results. After a large number of determinations of nitrogen evolved from a standard solution of urea, I found that the largest quantity was liberated by a solution containing the caustic soda and bromine in about the proportion recommended by Knop, but considerably more concentrated. A solution made up of 20 grams of caustic soda and 5 cc. of bromine, and anywhere from 50 to 100 cc. of water, gave fairly uniform results, and from five to ten per cent. more nitrogen than the more dilute solutions. In order to avoid as much as possible too rapid action and spurting, I prefer the solution made up with 100 cc. of water to the more concentrated. Even with this solution I was seldom able to obtain 92 per cent. of the known amount of nitrogen in a standard solution of urea.

In trying to find some method by which I could effect the complete decomposition of the urea and liberation of all the nitrogen, it occurred to me to mix the urea and the caustic soda solutions and then add the bromine. I hoped that by forming in this way the hypobromite in the presence of the urea to accomplish my purpose.

The first experiment with this method gave better results than I had at any time obtained in the old way. I then began a series of experiments to find how much of the nitrogen was liberated by this modification of Knop's method. The following table gives the results of a few of these:

No.	Amount of Urea.	Bar.	Temp.	Vol. of Nitrogen.	Weight of N.	Weight of Urea.	Per Ct.
1.	3 cc. 3 per ct. urea solution,	767	21°	36.35	41.75	89.47	99.40
2.	" " " "	767	21	36.30	41.70	89.36	99.29
3.	" " " "	767	21.5	36.50	41.82	89.62	99.57
4.	2 cc. " " "	767	21	24.20	27.80	59.56	99.29
5.	" " " "	767	21.8	24.30	27.80	59.56	99.29
6.	" " " "	765	21.5	24.45	27.94	59.88	99.77
7.	5 cc. 2 per ct. urea solution,	765	20.8	40.30	46.21	99.02	99.02
8.	" " " "	765	21	40.40	46.28	99.17	99.17
9.	" " " "	765	20	40.50	46.62	99.91	99.91
10.	3 cc. " " "	765	20.9	24.33	27.88	59.74	99.59
11.	" " " "	765	21	24.38	27.93	59.85	99.75
12.	" " " "	765	21	24.26	27.73	59.43	99.04
13.	7 cc. 1 per ct. urea solution,	765	21.6	28.40	32.44	69.52	99.30
14.	" " " "	765	22	28.40	32.37	69.37	99.10
15.	" " " "	765	22	28.60	32.60	69.86	99.79

The form of apparatus used in these experiments is the same as that generally used with the old method. It consists of a small flask or bottle, a specimen tube, a burette, and a tall glass cylinder. The flask is closed with a rubber stopper having two perforations. Through one of these passes a tube which is connected by rubber tubing to the burette. Through the other passes a short tube which opens externally, but may be closed by a pinchcock and a bit of rubber tubing. The tall cylinder is filled with water, and the burette inverted in it. The requisite quantities of the caustic soda and the urea solutions are placed in the flask, and the specimen tube, into which the bromine has been placed, is set in this, inclined against the side of the flask so that it will not overturn. The stopper being inserted, the flask is immersed in a large vessel of water whose temperature is noted, and allowed to remain until its temperature is constant. The burette is elevated until the level of the water is exactly at zero, and the pinchcock then closed. By tilting the flask to one side, the bromine may now be allowed to run slowly out and mix with the caustic soda and urea solutions.

The evolution of nitrogen takes place rapidly, and in a few minutes the reaction is completed. The flask should be shaken until all the bromine has disappeared. It is then replaced in the large vessel of water to reduce it to its original temperature. The burette being elevated until the water is at the same level inside and out, the volume of gas is read off and corrected for temperature and barometric pressure. About forty minutes are required for each determination. The burette should be allowed to remain elevated out of the water sufficiently long before reading for the inclosed gas to acquire the temperature of the surrounding atmosphere. In order to prevent any elevation of temperature in the water surrounding the flask by the reaction, I found it convenient to cool the flask in another vessel containing water of about the same temperature, before replacing it.

The caustic soda solution is made by dissolving 20 grams of sodium hydrate in 100 cc. of water. With each 20 cc. of this there should be used 1 cc. of bromine. In the series of experiments already given I used in each from 20 to 30 cc. of the caustic soda solution, and from 1 to 1.5 cc. of bromine. The relative amounts of caustic soda and bromine should not vary, but it is not necessary to be very exact in the quantities used. When determining urea in very dilute solutions, or in very small quantities, it would be advisable to use proportionately small quantities of the reagents.

The most troublesome part of the experiment is the measuring out of the bromine; but if a few drops of water be placed in the specimen tube it will float on top, and prevent, to a great extent, the escape of the bromine vapor.

For calculating results I have found the method given by Franklyn in his "Water Analysis" to be by far the best. The weight of nitrogen multiplied by 2.143 gives the amount of urea.

I expect in the future to apply this method to the determination of nitrogen in other organic compounds, as I think it probable that it will give as accurate results as with urea.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY, *March*, 1882.

ON THE TRANSFORMATION OF OZONE INTO OXYGEN BY HEAT.

By Ira Remsen.

It is known that when ozone is heated to about 200° it is converted into oxygen. Accepting the prevalent view concerning the nature of ozone, but two conceptions regarding this transformation appear at all probable. If the molecule of ozone contains three atoms, and that of oxygen two, then the transformation of the former into the latter by heat consists, first, in the partial decomposition of the molecule, either into a molecule and an atom of oxygen, or into free atoms only, and, second, in the recombination of the free atoms to form molecules of ordinary oxygen. Though the interval of time between the decomposition of the ozone and the formation of the oxygen molecules may be infinitesimal, there must apparently be this interval, and then the oxygen should be in its most active state with the powers that characterize nascent oxygen. But ozone itself, as is well known, is a strong oxidizing agent, so that to distinguish between nascent oxygen and ozone appears at first to be a very difficult problem. A recent interesting communication[1] by E. Baumann shows how this may be done, and I am hence led to describe an experiment which was performed in this laboratory some time since by Mr. P. H. Broun, the results of which are especially noteworthy, as they seem to throw some light on the processes involved in the transformation of ozone into oxygen under the influence of heat.

Southworth and I have shown[2] that ozone does not oxidize carbon monoxide. Baumann confirms this, and further proves that nascent oxygen, obtained by the action of palladium-hydrogen on oxygen, does transform the monoxide into the dioxide. This difference in the conduct of the two substances furnishes a means of distinguishing between them. If in any gaseous mixture there is ozone and no nascent oxygen, carbon monoxide will not be oxidized by it. On the other hand, if nascent oxygen be present, carbon monoxide will be converted into carbon dioxide.

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[1] Zeitschrift für physiologische Chemie, **5**, 244.

[2] American Journal of Science, **11**, 136; and Berichte der deutschen chemischen Gesellschaft, **8**, 1415.

Having proved beyond a doubt that carbon monoxide is not oxidized by ozone at the ordinary temperature, it remained to determine at what temperature the oxidation is effected. It seemed probable that this temperature would be below that at which ozone is transformed into oxygen, or, if not, then at least at the transformation temperature. Mr. Broun's experiments above referred to, led to what appears to me to be an astonishing result, viz., that carbon monoxide is not oxidized by ozone even at the temperature at which the ozone is transformed into oxygen. For various reasons the experiments were left in a somewhat unsatisfactory shape, and recently, at my suggestion, they have been repeated by Mr. E. H. Keiser. Every precaution was taken to avoid error, and the result reached fully confirms the conclusion just stated. Before discussing this result in its relations to the nature of the molecule of ozone, I will describe in detail the experiments which led to it.

A gasometer was filled with pure carbon monoxide, made from potassium ferrocyanide and sulphuric acid, and purified by passage through four wash-bottles containing caustic soda solution. Another gasometer was filled with pure oxygen. In the first experiments the oxygen was ozonized by means of a Siemens tube connected with an efficient induction coil. It was afterwards found, however, that much stronger ozone could be obtained by the use of Wright's tube connected with a Holtz electrical machine. It is hence only necessary to describe one of the experiments made with the latter form of apparatus. A slow current of oxygen from the gasometer was passed through three wash-bottles containing caustic soda solution, and then through the ozonizer. The ozone was tested and found to be unusually strong. The greatest care had to be taken to avoid the exposure of rubber to its action, as it required but momentary contact to effect the perforation of the rubber. The carbon monoxide was passed through wash-bottles containing caustic soda solution and finally through baryta water. The two gases were then brought together in a U-tube placed in an air-bath. After leaving the U-tube the gases passed through perfectly clear lime-water. The mixture in the U-tube was heated gradually to about 300°. Under these conditions the current of the gases was continued for an hour, and no precipitate was formed in the lime-water. Separate experiments were made for the purpose of determining how readily the ozone was destroyed, and it was found that, even when the thermometer in the U-tube indicated a temperature considerably below that stated as the decomposition temperature of ozone, and when highly ozonized oxygen was certainly passing into the U-tube, no ozone passed out, whether carbon monoxide was present or not in the tube at the same time. The experiment as above described was repeated several times, but always with the same result. One modification of the experiment should also be mentioned in this connection. In order to get as good ozone as possible, the ozonizer was filled with oxygen, and the current of gas then stopped. The oxygen was left in the tube for a minute or two, and then passed slowly into the heated U-tube containing the carbon monoxide. This interrupted current of oxygen was continued for about an hour, but no oxidation of carbon monoxide to the dioxide could be detected.

It is difficult to see how the fact thus established can be explained, if we accept the prevailing ideas concerning the nature of ozone, and its transformation into oxygen by heat That carbon monoxide can unite with oxygen when the latter is in proper condition is established. We cannot conceive of a more favorable condition for this union than that presented by free atoms of oxygen. When ozone passes into the form of oxygen under the influence of heat, are there not formed free atoms of oxygen? If not, then how does this change take place? If the molecule of ozone consists of an odd number of oxygen atoms, free atoms must apparently be formed during the change. We may, to be sure, conceive of the change as possibly taking place in this way. Two ozone molecules, after being partly broken up, may unite, forming a more complex molecule of six atoms, and this may then break up in pairs of atoms or into oxygen molecules. Even this would involve, as far as we can form any conception of such a process, a temporary increase in the activity of the oxygen. Speculation in this direction can, however, have but very little value at present.

Another thought suggests itself. Hoppe-Seyler and Baumann hold that the energetic oxidizing action of palladium-hydrogen and oxygen is due to the formation of nascent oxygen. While this explanation appears probable, it certainly lacks adequate proof. The action may be more complicated than this explanation would make it appear. On the other hand, Moritz Traube's statement[1] that the action is due to the formation of hydrogen dioxide would appear to be disproved by the fact that, while carbon monoxide is oxidized by palladium-hydrogen in the presence of oxygen, it is not oxidized by hydrogen dioxide, as was shown by me some time since.[2] The experiments upon which my statement on this point was originally based have been recently repeated in this laboratory by Mr. E. H. Keiser, and the result first stated shown to be correct. Even when carbon monoxide is passed into a solution of hydrogen dioxide which is undergoing rapid decomposition by heat, no oxidation is effected. This result is just as inexplicable as the negative result obtained with heated ozone.

Further experiments are called for to determine whether there are not conditions under which hydrogen dioxide can oxidize carbon monoxide. Possibly the presence of one of the many substances known to have the power to decompose the dioxide may at the same time increase its oxidizing power.

March, 1882.

NOTE ON THE VOLUMETRIC ESTIMATION OF ZINC, BY TITRATION WITH POTASSIUM FERROCYANIDE.

By Robert W. Mahon.

According to a method previously described for the volumetric estimation of zinc, a standard solution of potassium ferrocyanide is obtained by titrating a solution of known strength of pure zinc, dissolved in hydrochloric acid. After each addition of potassium ferrocyanide a drop of the solution is tested with a drop of a solution of uranium acetate, to ascertain whether the whole of the zinc has been converted into ferrocyanide, and an excess of the potassium ferrocyanide added. As soon as an excess of potassium ferrocyanide is added, a brown spot is obtained by bringing a drop of the solution in contact with a drop of uranium acetate solution. For the determination of zinc in its ores, they are dissolved in nitric and hydrochloric acids; and those metals whose sulphides are formed in acid solution are precipitated by sulphuretted hydrogen. After filtering, the iron is oxidized with nitric acid, and precipitated by addition of ammonium hydrate in excess, the zinc remaining in solution. The ammoniacal filtrate is made slightly acid, with hydrochloric acid, and, in the absence of manganese, is now ready for titration. In the case of Franklinite and other zinc ores containing manganese, this method for the estimation of zinc is not as easy of application as when manganese is not associated with zinc in the ore.

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[1] Berichte der deutschen chemischen Gesellschaft, 15, 222.

[2] Ibid. 9, 1876.

In the original paper describing the method, Fahlberg[1] directs that, after the separation of iron by excess of ammonia, the ammoniacal filtrate be made acid with excess of hydrochloric acid, and that the titration be made into this acid solution. The statement is made that the presence of manganese will not interfere with this titration. This statement I find to be erroneous. Both the manganese and zinc will be precipitated, even in a solution acid with hydrochloric acid. And, moreover, it is not possible to make the solution sufficiently acid to prevent such precipitation. When to a very dilute solution of a salt of manganese, in pure water, potassium ferrocyanide is added, the manganese is not at once precipitated. If ammonium chloride is present (the condition in the actual analysis), the precipitation will be more nearly instantaneous. When the quantity of manganese is considerable, the precipitation will occur at once, even in the absence of ammonium chloride.

The presence of manganese is then not allowable, even in small quantities, in the solution with zinc, where zinc is to be estimated by titration with potassium ferrocyanide. No way of precipitating manganese and leaving zinc in solution presents itself, as any precipitation of manganese by oxidation would necessarily carry down considerable quantities of zinc with it; such a precipitation, for example, as that of the oxides of manganese out of the solution of the acetate by addition of bromine water. This method for the separation of manganese and zinc, although frequently employed, is not permissible, as the precipitated oxides of manganese will carry down considerable quantities of zinc with them.

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[1] Zeitschrift für analytische Chemie, **13**, 379.

In order to get a solution for titration when manganese and zinc are associated in an ore, it is necessary to precipitate the zinc as sulphide out of the solution strongly acid with acetic acid by sulphuretted hydrogen, and to redissolve this precipitate in hydrochloric acid.

Dr. Fahlberg informs me that, since his communication above referred to, he has also observed the precipitation of manganese by potassium ferrocyanide in hydrochloric acid solution.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY, March, 1882.

REVIEWS AND REPORTS.

REPORT ON ANALYTICAL CHEMISTRY.

ARSENIC.—E. Lyttkens,[1] director of the Chemical Station at Halmstad, has made some interesting statements regarding the very frequent presence of arsenic in prints, carpets, shades, etc. Within two and a half years (1878, 1879 and the first half of 1880) 1704 samples of these materials were examined at the station, and 23.3 per cent. found to contain arsenic. In each of these cases the test was made with 150 square centimeters of the material; but a Swedish law, taking effect on the 1st of July, 1880, prescribes that materials shall be regarded as containing arsenic when "a black, or brown-black, partially indistinct arsenic mirror can be obtained in a tube 1.5 to 2 mm. in diameter from 440 square centimeters of printed, or 220 square centimeters of dyed samples." During the three following months 151 samples in the quantities prescribed by the law were examined, and 34.4 per cent. found to contain arsenic. It was found in prints of all colors. In the case of dyed materials, samples having brown and red colors; in the case of carpets, those having yellowish-brown and gray colors yielded it most frequently.

The method of examination employed consisted of the following steps: Oxidation of the sample by means of chlorate of potassium and dilute sulphuric acid; addition of sulphite of sodium to reduce any arsenic acid that may have formed; filtration; precipitation of the arsenic by sulphide of hydrogen; filtration after 12 hours; solution of the precipitate in warm carbonate of ammonium; evaporation of the solution to dryness; oxidation of the residue by means of chlorate of potassium and dilute sulphuric acid; evaporation to decompose and expel chlorine compounds; and, finally, reduction in Marsh's apparatus.

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[1] Versuchs-Stationen, **26**, 305.

To obtain the arsenic mirror from arsenious oxide or the sulphides of arsenic, Ch. Brame[1] heats the material with oxide of barium. A portion of the arsenic is liberated and forms a mirror, while the remainder is oxidized and unites with the barium. The presence of arsenic acid in the residue is demonstrated by dissolving in nitric acid and adding nitrate of silver. Similar but less striking results are obtained by using the oxide of calcium, potassium or sodium. Realgar and orpiment when treated in this way yield mirrors, but less easily than arsenious oxide. In the case of orpiment there is deflagration. If the mirror is treated with chlorine and the product exposed to atmospheric moisture, arsenic acid is formed, and its presence may be verified by means of nitrate of silver.

To avoid the well-known danger of reduction when arseniate of ammonium-magnesium is heated for the purpose of converting it into pyroarseniate of magnesium, F. Reichel[2] recommends moistening the precipitate with nitric acid.

W. Fresenius[3] has subjected the Fresenius-Babo[4] method of detecting arsenic to a critical examination and found that, when it is executed in exact accordance with the directions of its authors, it fully justifies all the claims which were made for it by them. The immediate occasion of the investigation was a description of the method in a much modified form in the latest edition of Graham-Otto's Inorganic Chemistry, the modifications relating in part to details which were especially emphasized in the original article as essential. In order to ascertain when and how the various modifications originated, all accessible works assuming to describe the method were compared. This examination led to the remarkable discovery that only four of these works—those of R. Fresenius, H. Will, Gorup-Besanez and Ph. Th. Büchner, give the method in its original and correct form. Further investigation revealed the fact that the modifications were first proposed in the various editions of Graham-Otto or of Otto's work on the detection of poisons, and that these works, rather than the original article, had been used as sources of information by those in whose books the method is incorrectly described. It appeared, furthermore, that opinions regarding the method had become unfavorable in proportion to the extent of its modification from the original form.

SILICON.—W. Hempel[5] recommends fusion with the subnitrate of bismuth as an effective method of decomposing silicates. 0.5 gram of the silicate is mixed with 10 grams of the bismuth compound and the mixture gently heated until the evolution of oxide of nitrogen fumes ceases. The temperature is then raised until the mass fuses, and the heating afterwards continued for about ten minutes. The molten material is poured into a platinum dish floating upon cold water, and after cooling, treated with hydrochloric acid. The solution is then evaporated to dryness, the residue treated with hydrochloric acid, and the silica separated by filtering and washing with acid. The bismuth is then removed by diluting with water and treating the filtrate from the oxychloride with sulphide of hydrogen.

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[1] Comptes Rendus, **92**, 188.

[2] Zeitsch. für analyt. Chemie, 1881, 89.

[3] Zeitsch. für analyt. Chemie, 1881, 522.

[4] Liebig's Annalen, **49**, 287.

[5] Zeitsch. für analyt. Chemie, 1881, 496.

M. W. Iles[1] recommends for the same purpose, especially for the decomposition of slags containing lead, fusion with potassium hydroxide in silver crucibles. W. Bettel[2] advocates the use of gold-lined platinum crucibles for such fusions with potassium hydroxide.

CARBON.—A. Muntz and E. Aubin[3] propose what appears to be an excellent method for the collection, and preservation for future estimation, of the carbonic acid of the air. For this purpose glass tubes, drawn out at both ends and containing pumice-stone saturated with caustic potassa, which is free from carbonate, are sealed before the blowpipe. The tubes thus prepared at the laboratory are opened at the place where the air is to be tested, a measured volume of air aspirated through them, and again sealed. Whenever it is desired to determine the carbonic acid thus collected, one end of the glass tube containing it is placed in connection with a mercury air-pump and eudiometer, and after a partial vacuum has been established, dilute sulphuric acid is admitted at the other end. The carbonic acid is then estimated by absorption.

ELECTROLYTIC DETERMINATIONS AND SEPARATIONS.—A Classen and M. A. von Reis[4] have found that accurate quantitative determinations and separations can be effected in the case of quite a number of metals by subjecting their double alkaline oxalates to electrolysis. The metals which can be thus determined and separated either from each other or from other elements are cobalt, nickel, iron, zinc, manganese, bismuth, lead, copper, cadmium, tin and antimony.

1. *Cobalt.*—The solution is treated with sufficient oxalate of ammonium to form the double salt; heated; three or four grams of solid oxalate ammonium added; and while still hot, subjected to electrolysis. When the metal has been completely precipitated, the positive electrode is removed, the liquid poured off, and the precipitate washed—first with water, then with alcohol, and finally with absolute ether. The arrangement of electrodes preferred by the authors consists of a flat platinum dish to contain the liquid and receive the deposit, and a platinum disk attached at its center to a stout platinum wire. A battery of two Bunsen's cells is recommended.

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[1] Chemical News, **43**, 78.

[2] Chemical News, **43**, 94.

[3] Comptes Rendus, **92**, 247.

[4] Berichte der deutsch. chem. Gesellschaft, **14**, 1622.

2. *Nickel.*—The precipitation is effected in precisely the same manner as that of cobalt.

3. *Iron* is quickly and completely precipitated—provided a sufficient excess of the oxalate of ammonium is added—as a brilliant, steel-gray, perfectly adherent coating, which may be exposed to the air for several days without undergoing perceptible oxidation.

4. *Zinc* precipitates as satisfactorily as the preceding metals. The deposit cannot, however, be readily removed from the platinum by means of acids. It is necessary to ignite the residue which does not dissolve, and then repeat the treatment with an acid.

5. *Manganese*, if oxalate of potassium instead of the ammonium salt is used, is completely precipitated upon the positive pole as superoxide, but the precipitate adheres so loosely that it must be collected upon a filter and determined as tetroxide. It is not completely precipitated from solutions containing oxalate of ammonium.

6. *Bismuth* can be precipitated from the oxalate of ammonium solution; and, if a large platinum dish is used, the deposit is sufficiently compact to admit of washing.

7. *Lead* is precipitated, but is oxidized so rapidly in contact with the air that its determination by this method cannot be recommended.

8. *Copper* is readily precipitated from solutions containing a considerable excess of the oxalate of ammonium, provided a strong current (one equivalent to 330 cc. of electrolytic gas per hour) is employed.

9. *Cadmium* precipitates, and the deposit adheres well enough to admit of careful washing.

10. *Tin* can be deposited either from the double ammonium oxalate or from its solution in hydrochloric acid. There is, however, some difficulty in removing the deposit from the platinum.

11. *Antimony* can be precipitated from the double potassium oxalate or its solution in hydrochloric acid, but not in compact condition. The addition of an alkaline tartrate gives a firmly adhering deposit, but greatly retards the precipitation. Good results are, however, obtained by precipitating from the double sulphide of antimony and ammonium. The solution, which may contain an excess of hydrochloric acid, is saturated with sulphide of hydrogen, neutralized with ammonia, and then treated with an excess of sulphide of ammonium. From this solution the antimony separates as a fine, light-gray coating, which adheres firmly to the platinum, if the precipitation is not too rapid.

12. *Separation of Iron and Manganese.*—The solution is prepared in the same manner as for the precipitation of cobalt, nickel or iron, by adding an excess of oxalate of ammonium, heating, and then dissolving in it 3 or 4 grams of the solid oxalate. The iron is completely precipitated, and perfectly separated from the manganese, provided the proportion of the latter is not too large. If the quantity of manganese is twice that of the iron, or greater, the separation is imperfect. The difficulty can be remedied by adding

oxalic acid (without interrupting the current) until the manganese precipitate is dissolved. There precipitation of the manganese is attended with a perfect separation of the two metals.

13. *Separation of Iron and Aluminium.*—The neutral or slightly acid solution is treated with an excess of ammonium oxalate, and 2 or 3 grams of the solid oxalate added for every 0.100 gram of oxides of iron and aluminium. It is then heated, and while hot subjected to electrolysis. The iron precipitates completely; but the aluminium remains in solution until the quantity of carbonate of ammonium, formed by the decomposition of the oxalate, exceeds that of the remaining oxalate of ammonium, when the precipitation of aluminium as hydroxide begins. The solution is tested from time to time for iron, and the current interrupted as soon as possible after the last traces of it have disappeared. The separation is complete when the quantity of aluminium does not exceed that of the iron, otherwise the precipitate of aluminium hydroxide must be dissolved with oxalic acid, as in the case of the separation of iron and manganese, and then allowed to reform.

In a separate publication entitled "Quantitative Analyse auf electrolytischem Wege," Classen gives detailed directions for the application of his method of electrolysis to the analysis of nearly fifty alloys, ores and metallurgical products.

METALS AND ALKALIES.—W. Bachmeyer[1] recommends a solution of tannin as a sensitive reagent for caustic alkalies. A distinct red or reddish-brown color, which is transformed after a time into a dirty green, is produced. By means of this reaction one part of a caustic alkali in 1,000,000 parts of water can be detected. It also serves for the detection of minute quantities of the neutral carbonates of the alkalies. The other salts of the alkalies produce no visible effect on the solution of tannin.

According to L. L. de Koninck[2] the double nitrite of cobalt and sodium, prepared by adding the chloride of cobalt and acetic acid to a 10 per cent. solution of sodium nitrite, is a more sensitive reagent for the detection of potassium than the chloride of platinum. It gives an immediate precipitate in a solution containing one per cent. of potassium chloride, and a precipitate after some time in a solution which is ten times as dilute.

In addition to the numerous impurities—such as chlorides, sulphates, nitrites, cyanides, sulphocyanides, &c., which have been found in the sodium hydroxide of commerce since its manufacture directly from the red lye of the soda process has been introduced, E. Donath[3] has detected arsenic and vanadium. These impurities, he states, must have been introduced through the sulphuric acid employed in the process.

To separate lithium from large quantities of potassium and sodium, W. F. Gintl[4] makes use of the difference in solubility of their chlorides in strong hydrochloric acid. The mixture of dried chlorides is digested for two hours upon the water-bath with four or five volumes of strong hydrochloric acid, with replacement from time to time of the evaporated acid. After cooling, the solution is decanted through a filter of glass wool which has been thoroughly washed with strong acid. The same treatment is twice repeated with the residue, which is then brought upon the filter and washed with strong hydrochloric acid until the filtrate is free from lithium. The filtrate is evaporated to one-twentieth of its volume, treated with three volumes of strong hydrochloric acid, and filtered. The residue is then washed, as before, with strong hydrochloric acid. The final filtrate contains all the lithium and very little potassium or sodium.

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[1] Zeitschrift für analyt. Chemie, 1881, 234.

[2] Zeitschrift für analyt. Chemie, 1881, 390

[3] Dingler's polytech. Journal, **240**, 318.

[4] Dingler's polytech. Journal, **240**, 83.

H. N. Morse.

On a Possible new Kind of Isomerism.

As is well known, isomerism in the usual sense has nothing to do with the kind of union existing between the atoms which form a molecule. If, in a given compound, it can be shown what connections exists between the atoms; if it can be shown that this carbon atom is in union with that hydrogen, and this oxygen atom with that carbon atom, and so on until all the connections are pointed out, then we say the structure of the compound is determined; and, in an isomeric compound, the connections between the atoms must be different, or, what is the same thing, different atoms must be united.

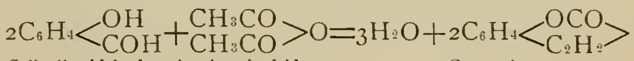
A second kind of isomerism, according to the hypothesis of Le Bel and Van't Hoff, is possible in two compounds in which the same atomic connections exist. In any compound in which there is a carbon atom, four bonds of which are satisfied with four unlike atoms or groups, we can conceive these four groups arranged in space in two ways. Imagining the carbon atom to be situated in the centre of a tetrahedron, and the four unlike groups or atoms at the four angles of the tetrahedron, then the groups may be arranged in such a way as to form one of the two possible tetrahedra, or in such a way as to give the complementary tetrahedron. The isomerism is here due not to different connections, but to different arrangement of the atoms in space around the carbon atom.

A third kind of isomerism is suggested by some formulas in common use. We speak of single and double linkage and represent these conditions by single and double lines. We can conceive of a kind of isomerism represented by the two formulas $CH_2—CH_2$ and $CH_2=CH_2$. In such a case the isomerism would be due to a difference in the kind of union existing between the carbon atoms. No such cases have thus far been observed.

Whether they are possible or not is not known, nor is it by any means certain that there is such a condition as that which is called double linkage, if by the expression is meant what the formula implies—union by twice the force that operates in single linkage.

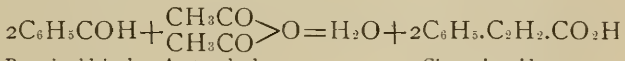
Some investigations of W. H. PERKIN which have been carried on for the past seven years seem to lead to the conclusion that isomerism may be due to a cause hitherto not considered. This new kind of isomerism is the simplest, and it increases apparently the number of possibilities to an infinite extent. It is due to *differences in the distances between atoms.* Accepting the suggestion of Perkin, we might have isomerides of every known compound. Thus there might be a sodium chloride Na—Cl in which the atoms are near together, and another Na——Cl in which the atoms are more widely separated; and indeed, carrying out the idea, we might apparently have an infinite number of varieties of every chemical compound. Judging from the facts in our possession, it is not probable, however, that the above kind of isomerism is common, and for this we may be thankful. A brief account of Perkin's papers is here given.

Some years ago he showed that when the sodium compound of salicylic aldehyde and acetic anhydride are brought together, coumarin, a substance occurring in nature in the Tonka bean, is formed. Since that time several attempts have been made to explain the reaction, and it is in connection with this work that the observations under consideration were made. As regards the reaction involved in the formation of coumarin, it may be said that it is somewhat like that which takes place between benzoic aldehyde and acetic anhydride, resulting in the formation of cinnamic acid. The two reactions are represented thus :



$$2C_6H_4<\begin{matrix}OH\\COH\end{matrix}+\begin{matrix}CH_3CO\\CH_3CO\end{matrix}>O=3H_2O+2C_6H_4<\begin{matrix}OCO\\C_2H_2\end{matrix}>$$

Salicylic aldehyde. Acetic anhydride. Coumarin.

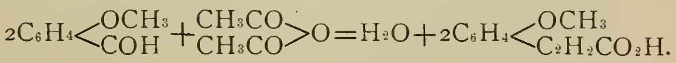


$$2C_6H_5COH+\begin{matrix}CH_3CO\\CH_3CO\end{matrix}>O=H_2O+2C_6H_5.C_2H_2.CO_2H$$

Benzoic aldehyde. Acet. anhyd. Cinnamic acid.

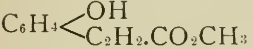
Coumarin is the anhydride of coumaric acid, the formula of which is $C_6H_4<\begin{matrix}OH\\C_2H_2.CO_2H\end{matrix}$.

When methylsalicylic aldehyde is treated with acetic anhydride this reaction takes place:



$$2C_6H_4<\begin{matrix}OCH_3\\COH\end{matrix}+\begin{matrix}CH_3CO\\CH_3CO\end{matrix}>O=H_2O+2C_6H_4<\begin{matrix}OCH_3\\C_2H_2CO_2H.\end{matrix}$$

The change in this case is confined to the aldehyde group, the group OCH_3 remaining unchanged. The product is called *β-methylorthoxyphenylacrylic acid.*

Now when the sodium derivative of coumarin, obtained by boiling coumarin with sodium hydroxide, was treated with enough methyl iodide to combine with *half* the sodium, and the resulting compound treated with hydrochloric acid, a new acid was obtained, the analysis of which showed the formula to be $C_{10}H_{10}O_3$. It is identical in composition with the β-acid above mentioned, and is called *α-methylorthoxyphenylacrylic acid.* The two isomeric substances differ very markedly in their properties. Assuming the sodium derivative of coumarin to have the constitution expressed by the formula $C_6H_4<\begin{matrix}ONa\\C_2H_2\end{matrix}CO_2Na$, by treatment with enough methyl iodide to combine with half the sodium we would obtain either $C_6H_4<\begin{matrix}ONa\\C_2H_2.CO_2CH_3\end{matrix}$ or $C_6H_4<\begin{matrix}OCH_3\\C_2H_2CO_2Na\end{matrix}$; and from these compounds by treatment with hydrochloric acid either  $C_6H_4<\begin{matrix}OH\\C_2H_2.CO_2CH_3\end{matrix}$ or $C_6H_4<\begin{matrix}OCH_3\\C_2H_2CO_2H\end{matrix}$. It might be thought at first that the difference between the α- and β- acids consists in the fact that in one the methyl group is in the phenol hydroxyl, and in the other in the carboxyl. That this is not so is proved by a careful consideration of all the facts. In the course of an elaborate and interesting argument Perkin shows: (1) That both acids have the formula $C_6H_4<\begin{matrix}OCH_3\\C_2H_2.CO_2H\end{matrix}$; (2) that both are ortho compounds; and (3) that the group C_2H_2 is the same in both. Compounds corresponding to the α- and β-acids have been obtained from homologues of coumarin, as from propionic and butyric coumarins.

Summing up all the evidence at command, the conclusion is reached that "this isomerism cannot be explained by any ordinary kind of chemical constitutional formula we have at present." Comparing the physical properties of the corresponding members of the two series of isomeric compounds, we find: that the boiling points of the α-compounds are always the lower; that the densities of the α-compounds are lower than those of the β-compounds; that "the magnetic rotary power of the methylic α- and β-methylorthoxyphenylacrylates shows a difference in the same direction, the α giving a lower result than the β, considerably greater than the variations of the densities would account for."

"*These facts would seem to indicate that in the α- compounds the groups, or some of them, contained in the molecules are farther apart than in the β- compounds.*"

"There is one point connected with this matter of isomerism worthy of note, and that is, that the changes of condition which these bodies undergo are always associated with *dehydration* and *rehydration.* Thus β-coumaric acid on losing the elements of a molecule of water becomes coumarin. This when hydrated does not go back to β-coumaric acid, but to its unstable isomeride α-coumaric acid, and it is not until this (or rather its salt) is strongly heated that the original acid is reproduced. The difference in stability between α and β compounds is also seen to be in connection with the hydroxyl. These remarks also apply to the cases of maleic and fumaric acids, and citraconic and mesaconic acids, where we find the formation of maleic or citraconic resulting from the removal of a molecule of water from fumaric or mesaconic acids and rehydration of the product.

"It may be remarked in passing, that nearly all the bodies which are now called physical isomerides are hydroxylized products, and those containing the largest number of hydroxyls have the largest number of these isomerides, as in the case of the carbohydrates."

In the last paper published in connection with this line of investigation, Perkin gives an account of experiments on citraconic and mesaconic ethers, and maleic and fumaric acids, and arrives at the interesting conclusion that "there is but one anhydride for maleic and fumaric acids, one anhydride for citraconic and mesaconic acids, and one anhydride for α- and β-coumaric acids."

He concludes that the isomerism of these acids can be due to nothing else than a difference in the relationship of the hydroxyl to the radicals.—(*Journal of the Chem. Soc.*, 1877, p. 388–427; 1881, p. 409–452; 1881, p. 554–562).

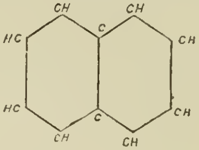
QUINOLINE AND ITS RECENT SYNTHETICAL FORMATION.

Although this substance has long been known to chemists, the interest attaching to it has been, until comparatively recently, purely scientific rather than practical. Skraup's demonstration, however, that it can be synthetically prepared on a scale sufficiently large for commercial purposes, together with the fact that it bears a close resemblance to quinine in physiological effects, and that it has already come into use as a remedial agent under the name of "artificial quinine," has brought it into prominence.

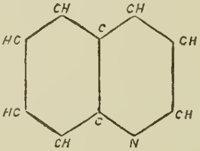
Quinoline belongs to the class of carbon compounds known as the "alkaloids," a group of bodies so called on account of their basic properties, *i. e.* their power of combining with acids to form salts. All alkaloids contain carbon, hydrogen and nitrogen; most of them contain, in addition to these three elements, oxygen. They resemble in their general properties the alkalies, but are more strictly analogous to ammonia than to the so-called fixed alkalies, as their combination with acids is direct without the formation of water. Quinoline forms the first member of an homologous series of alkaloids known as the *quinoline series*, the members of which correspond to the general formula $C_nH_{2n-11}N$, the formula of quinoline being C_9H_7N. The best known of the remaining members of the series are lepidine, $C_{10}H_9N$, and cryptidine, $C_{11}H_{11}N$.

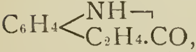
This series of alkaloids may be obtained by the distillation of several alkaloids which occur in nature, *i. e.* by the distillation of quinine, cinchonine, strychnine. Quinoline may also be obtained from coal-tar, but the labor involved in this method is very great. As a result of the preparation of this substance on the large scale, a vigorous effort is at present being made to introduce it into medicine, on account of its agreeable character and cheapness, as a substitute for quinine. It will not, therefore, be out of place to present a short history of quinoline, and of the various syntheses made, all of which have tended to throw light upon the structure of the body, but which, owing to the small yields obtained, are, with the exception of Skraup's method, only of scientific interest.

Körner's hypothesis of the structure of quinoline was a valuable one, in that it suggested to other investigators reactions by which it could be produced. This hypothesis assumes that quinoline is naphthalene in which a CH group is replaced by an atom of nitrogen, thus naphthalene is represented by the formula



and quinoline by the formula



Baeyer's synthesis[1] of quinoline from hydrocarbostyril,  $C_6H_4<\begin{matrix}NH\text{—}\urcorner\\C_2H_4.CO\end{matrix}$, furnished the experimental basis for Körner's formula. König's synthesis[2] from allylaniline also furnishes some support for the same formula.

Skraup's synthesis[3] was suggested by a consideration of Graebe's work on alizarin blue. Graebe found that alizarin blue can be produced from nitroalizarin and glycerin, these substances acting upon each other under the proper conditions according to the following equation:

$$\underset{\text{Nitroalizarin.}}{C_{14}H_7(NO_2)O_4}+\underset{\text{Glycerin.}}{C_3H_8O_3}=\underset{\text{Alizarin blue.}}{C_{17}H_9NO_4}+3H_2O+O_2.$$

Graebe believed that alizarin blue is a substance allied in chemical structure to quinoline. Skraup then assumed that, if Graebe's opinion were true, the formation of quinoline from nitrobenzene should result by a reaction analogous to the above in which nitroalizarine is replaced by nitrobenzene. He also assumed that the homologues of quinoline should in like manner be formed by the action of glycerin upon substituted nitrobenzenes. These opinions were substantiated by experiment. In the above equation it is noticeable that free oxygen is evolved, and to the action of this element both Graebe and Skraup ascribed the formation, together with alizarin blue, of an undesirable brown-colored by-product. To avoid this destructive action of oxygen on the products, the presence of a reducing agent was considered necessary, and, in the case of the formation of quinoline, Skraup regarded the amide compound, $C_6H_5NH_2$, *i. e.* aniline, corresponding to the nitro compound $C_6H_5NO_2$, as the agent best suited for reducing purposes.

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[1] Berichte der deutschen chemischen Gesellschaft, 12, 1320.

[2] Ibid. 12, 453.

[3] Monatshefte für Chemie, Feb. 1881.

The reaction analogous to the above, by which quinoline is formed, is as follows:

$$\underset{\text{Nitrobenzene.}}{C_6H_5NO_2}+\underset{\text{Glycerin.}}{C_3H_8O_3}=\underset{\text{Quinoline.}}{C_9H_7N}+3H_2O+O_2.$$

Skraup believed that a reaction would also take place directly between aniline and glycerin thus:

$$\underset{\text{Aniline.}}{C_6H_5NH_2}+\underset{\text{Glycerin.}}{C_3H_8O_3}=\underset{\text{Quinoline.}}{C_9H_7N}+3H_2O+H_2.$$

These two reactions may be expressed in one:

$$\underset{\text{Aniline.}}{2C_6H_7N}+\underset{\text{Nitrobenzene.}}{C_6H_5NO_2}+\underset{\text{Glycerin.}}{3C_3H_8O_3}=3C_9H_7N+11H_2O.$$

We see then that aniline has in this reaction a double function, *i. e.* it neutralizes the destructive effect of oxygen and also contributes directly to the formation of quinoline. This double function of aniline has been clearly substantiated by experiment. In the formation of quinoline by this method the presence of sulphuric acid is necessary as a dehydrating agent. Skraup gives the following directions for the process: 24 grams nitrobenzene, 38 grams aniline and 120 grams glycerin are mixed with 100 grams oil of vitriol in a 2 litre retort; the mass, which has become warm, is shaken up until the aniline sulphate is perfectly dissolved, and is then heated on a sand bath, a long inverted condenser being also employed. At the beginning, the operation must be carefully watched in order to regulate the action, which is violent. Full details of the process are given in Skraup's paper to which reference is above made. The yield in raw quinoline by this process is from 70 to 75 per cent. of the weight of the mixture of aniline and nitrobenzene, that is about 60 per cent. of the amount theoretically possible is obtained. Quinoline thus obtained agrees, according to Skraup, perfectly with that obtained from cinchoninic acid.

The physiological effects of quinoline have already been investigated to a considerable extent, experiments having originally been made upon animals, and later on human beings, both in health and in sickness. Donath has occupied himself with the study of quinoline in its physiological action, and has announced its similarity to quinine. Loewy has reported in the *Vienna Medical Press* a number of cases successfully treated by means of quinoline. Salkowsky, of St. Petersburg, also gives a favorable report. It is stated that none of the inconveniences attendant upon the use of quinine, such as dizziness, loss of hearing, etc., are noticed when quinoline is employed.

The evidence as to the value of quinoline as a curative agent must still, however, be considered as incomplete; but, owing to the importance of this question, a satisfactory solution will probably not long be wanting. W. C. D.

THE JOURNAL OF THE SOCIETY OF CHEMICAL INDUSTRY: A MONTHLY RECORD FOR ALL INTERESTED IN CHEMICAL MANUFACTURES. No. 1, Vol. I. January, 1882.

About a year ago the Society of Chemical Industry was inaugurated in England with these objects:

"To advance Applied Chemistry in all its branches.

"To promote the acquisition and practice of that species of knowledge which constitutes the profession of a Chemical Engineer.

"To enable all persons interested in Applied Chemistry to meet and to correspond; to facilitate the interchange of ideas respecting improvements in the various branches of chemical manufacture; and to publish and communicate information on such subjects."

Prof. Roscoe was elected president, and among the vice-presidents are Abel, Lowthian-Bell, Muspratt, Pattinson, Perkin, Siemens, Weldon, Williamson. Other distinguished names are found in the list of the members of the committee. With such men taking active part in the workings of the society it can not help being a success. The Society has now started a journal. Watson Smith of Owens College is the editor, acting under instructions from the publication committee, of which Prof. Roscoe is the chairman. The first number of the journal contains interesting matter, and if the standard is maintained, it will certainly be a valuable addition to the literature of Applied Chemistry. The principal contents of the number are: Professor Abel's address at the opening meeting of the Metropolitan Section of the Society; Specific Gravity Tables by Dr. Messel; Dynamic Theory of Manufacture of Sulphuric Acid, by F. Hunter; Society of German Alkali Makers: Report by Prof. Lunge; on Artificial Indigo, by Profs. H. E. Roscoe and A. Baeyer.

NOTES.

On Artificial Indigo.

Prof. Roscoe writes in *The Journal of the Society of Chemical Industry*, No. 1, Vol. I.: "As supplementing the information on this interesting subject contained in my lecture,[1] delivered at the Royal Institution in May last, I have now the pleasure of adding the following particulars of Professor Baeyer's observations on his visit to the manufactory of artificial indigo in November last. This shows that the production of artificial indigo is making progress; and I may add that the manufacture is being carried on up to the present day in the manner described by him. It appears, however, that the consumption of propiolic acid is at present limited to a few print works, whose chemists have successfully overcome the difficulties of its application. Let us hope that the great majority of English calico printers will soon follow in the wake of the pioneers. The important question referred to by Professor Baeyer in his letter, viz. that of finding a useful employment for para-nitro-cinnamic acid, now a waste product in the manufacture of propiolic acid—may possibly receive a solution from the recent researches of Otto Fischer on the synthesis of the rosaniline dyes, by means of para-nitro-benzaldehyde, a body obtained by the limited oxidation of para-nitro-cinnamic acid. Another point which requires attention is the loss of material incurred in the passage from propiolic acid to indigo. If this loss can be avoided, and if a use is found for the para acid, there seems no reason why indigo blue should not be itself obtained in course of time by Baeyer's reactions, particularly as cinnamic acid can now be made in any quantity, and at a very low price.

"That these researches are only the first steps in the production of colors from the indigo group of compounds is shown by the fact that Professor Baeyer, in February last, patented the production of another coloring matter, termed by him 'indoin.' This resembles indigo in color, and is obtained by the action of concentrated sulphuric acid upon ortho-nitro-phenyl-propiolic acid, when isatogenic acid is formed, and this is converted into the coloring matter by the action of ferrous sulphate. The soluble sulphurous acid compound of indoin is remarkable, and may become useful as a dye."

The following extracts from Professor Baeyer's letter will be of interest: "Propiolic acid is at this moment made at Ludwigshafen with the same degree of certainty as is attached to the preparation of any inorganic compound. . . . The first necessity in the technical preparation of propiolic acid is a cheap cinnamic acid. Your celebrated countryman, Perkin, was the first to make this acid by a simple reaction, viz. by heating bitter almond oil with acetic anhydride and acetate of soda. The Baden company simplified this reaction, as far as it can be simplified, and prepared cinnamic acid directly by fusing benzyl chloride with acetate of soda, and thus obtaining the acid without using either acetic anhydride or oil of bitter almonds. This reaction is carried on in large boilers fitted with mechanical stirrers, and gives a very satisfactory yield. Great difficulties were met with in nitrating cinnamic acid; but, thanks to the ability and patience of the chemists to the Baden company, these difficulties have been overcome, and a process has been found by which the operation can be conducted on any wished for scale, and with good results. I was amazed to see hundredweights of cinnamic acid undergoing the operation of treatment with nitric acid, for I remembered how difficult a task it was to work up a single pound in the laboratory. The preparation of ortho-nitro-cinnamic acid is carried out, first, by the conversion of cinnamic acid into its ethyl ether. The liquid ether is then allowed to run in a thin stream, together with the requisite quantity of a mixture of nitric and sulphuric acids, into a well-cooled vessel furnished with a stirring apparatus. The solid mixture of ortho and para-nitro-cinnamic ethers thus obtained is heated with alcohol, when the para-nitro-cinnamic ether remains undissolved, the ortho ether being dissolved, and deposited from the alcoholic solution in large yellowish crystals. This compound, on saponification, yields ortho-nitro-cinnamic acid. The conversion of this acid into ortho-nitro-phenyl-propiolic acid is carried out in two consecutive operations, both of which work well. The ortho acid is first acted on by bromine, by which means the dibromide is formed, and this is then dissolved in caustic-soda ley, when the soda salt of propiolic acid is formed. Propiolic acid itself is precipitated from the solution of the soda salt by means of an acid, and, after washing, it is sent to market as a paste. Artificial indigo is not itself manufactured in the works, the coloring matter being deposited by the printer himself in the fibre of the cloth from propiolic acid, as is aniline black from aniline. For this purpose a mixture of propiolic acid and xanthate of soda, to which a proper amount of thickening has been added, is printed on the cloth. The color makes its appearance on exposure to the air (ageing). It is found to be fast, and exhibits the characteristic tints of indigo in both light and dark shades.

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[1] See this Journal, 3, 282.

"The series of operations necessary for passing from toluene to indigo blue are, as is seen, rather long, but each process works so regularly and well that the preparation of propiolic acid and its conversion into indigo blue can be carried out with perfect ease. The only serious imperfection in the process is the loss of 40 per cent. of the cinnamic acid in the form of para-nitro-cinnamic ether. This will, it is to be hoped, be overcome by the employment of the compound for some useful purpose. On my visit to Ludwigshafen last November, I found the manufacture of indigo in full activity—200 kilograms of propiolic acid paste, containing 25 per cent. of the dry acid, were produced every day, and this is sold at the price of 10 shillings the kilogram."

Levulose.

Levulose has for a long time been distinguished by the name of uncrystallizable sugar, and, although it has been the subject of much investigation, it has hitherto never been isolated in a satisfactory state of purity, and the physical properties which have been attributed to it have either been observed with very impure specimens of levulose, or, oftener, deduced from the differences between the properties of glucose and those of the mixture of glucose and levulose known by the name of inverted sugar.

Jungfleisch and Lefranc have now succeeded in preparing pure levulose in crystalline form and have studied its properties. Inuline was selected by them as the most advantageous starting point, from the fact that it yields levulose alone, by complete saccharification. A solution of inuline in water, containing several thousandths of sulphuric acid added in the form of titrated solution, was heated to 100° for one hour, and, after cooling, the sulphuric acid removed from the solution by the addition of an amount of titrated baryta-water equivalent to the amount of acid used. The solution was then decolorized with animal charcoal, filtered, and the filtrate evaporated upon the water-bath *in vacuo* to a syrupy consistence. The solution if now left to itself would retain the syrupy form indefinitely, and, on the other hand, if dessicated over sulphuric acid, would lose more or less water and be converted into a solid, vitreous, hygroscopic mass. The great difficulty consists, then, in the removal of water from the solution without the transformation of the levulose into dehydration products which very readily takes place. This was accomplished by treating the syrupy residue with cold absolute alcohol, which only dissolves a slight trace of the saccharine matter, but abstracts water as well as certain impurities. After several washings with absolute alcohol, the insoluble portion was placed in a carefully closed vessel and left to itself in a cool place. Gradually fine needle-shaped crystals analogous to crystals of mannite made their appearance, and finally the entire mass assumed crystalline form. This crystallization was found to be effected more rapidly and more surely if a crystal of levulose previously obtained be added to the solution.

In order to decide the question which has been several times discussed of late as to the identity of levulose from inuline with that of inverted sugar, levulose was prepared from inverted sugar by a modification of the method of Dubrunfaut. Pure crystallized levulosate of calcium was decomposed under water by means of oxalic acid, and the solution of levulose thus obtained treated as described above by evaporation to syrupy consistence and washing with absolute alcohol. Levulose obtained in this manner was found to be in every respect identical with that from inuline. There is then but one variety of levulose and the name of uncrystallizable sugar should no longer be applied to it.

Levulose crystallized from alcoholic solution consists of fine colorless silky needles, which sometimes attain the length of 10 mm. and which usually radiate from a central point forming spherical groups. When freed from mother-liquor and dried over sulphuric acid, their composition is represented by the formula $C_6H_{12}O_6$. When moistened with alcohol and exposed to the air, levulose is deliquescent, but when perfectly dry it is very slightly hygroscopic, and only increases from one to two per cent. in weight when exposed to the air for several days. It fuses at about 95°, and at 100° loses water gradually, yielding ether derivatives. As would be expected from the optical properties of inverted sugar, the rotatory power of levulose varies very rapidly with the temperature; it also varies in a still greater degree with the dilution of the solution. MM. Jungfleisch and Lefranc announce their intention of continuing their investigations of this subject.—(*Comptes rendus*, 93, 54). R. D. C.

On a new Series of Bases derived from Morphine.

Since the transformation of morphine into codeine, an account of which has already been given, E. GRIMAUX has continued his investigations on morphine, and has succeeded in obtaining from it a new series of bases. When codeine or the sodium derivative of morphine is treated with methyl iodide, there is obtained, as has been shown, the iodomethylate of codeine, which possesses the properties of a quaternary iodide of ammonium. If now this be treated with silver oxide, there is obtained, not the corresponding hydrate of ammonium, but, by simple concentration on the water-bath, it is transformed into a solid and crystallizable tertiary base. This base is slightly soluble in water, easily soluble in alcohol and ether, and crystallizes from its alcoholic solution in brilliant needles which fuse at 118.5°. It is precipitated from its salts by potash and by ammonia, differing in this respect from codeine and codethyline, which ammonia does not precipitate. It gives with sulphuric acid a characteristic reaction. The concentrated acid colors it brown, then by the addition of a few drops of water it dissolves, forming a solution of intense blue-violet color. A further addition of water changes the color to clear red and then destroys it completely. This reaction is exactly like that given by cryptopine. The new base appears to be formed by the abstraction of a molecule of water from the quaternary hydrate of ammonium, and to constitute methocodeine, $C_{18}H_{20}NO_2(OCH_3)$, an isomer of codethyline, $C_{17}H_{18}NO_2(OC_2H_5)$. Claus has shown that by treatment with potash the quaternary iodides of ammonium derived from cinchonine and cinchonidine yield tertiary bases with loss of the elements of hydriodic acid in such a manner that the alcoholic group, at first in combination with nitrogen in the ammonium iodide, finally enters into combination with the hydrocarbon radical. It appeared to M. Grimaux that the formation of methocodeine, being due to a reaction of the same class, should take place under the same conditions; and he found, in fact, that when iodomethylate of codeine was boiled with an aqueous solution of potash, methocodeine was produced. The yield, however, was much better with silver oxide, in which case the transformation takes place below 100°. In order to generalize this reaction, iodomethylate of codethyline was also prepared and treated with silver oxide and with potash, and by this means a tertiary crystallizable base obtained, fusing at 132°, resembling methocodeine, but less soluble in ether, and giving with sulphuric acid the same violet coloration. This base has not been analyzed as yet, but is in all probability methocodethyline, $C_{18}H_{21}NO_2(OC_2H_5)$. This is then a general reaction by means of which there can be obtained homologues of codeine containing new alcoholic groups, not in the phenol hydroxyl of the morphine, but in the hydrocarbon radical of the morphine itself. It is in this manner that methocodeine is, as has been said above, isomeric with codethyline:

Methocodeine.	Codethyline.
$C_{18}H_{20}NO_2(OCH_3)$	$C_{17}H_{18}NO_2(OC_2H_5)$.

—(*Comptes rendus*, **93**, 591). R. D. C.

On the Proportions of Carbonic Acid in the higher Regions of the Atmosphere.

A. MUNTZ and E. AUBIN have recently made determinations of the proportions of carbonic acid in the atmosphere both in the city of Paris and in the open country near Vincennes, the results of which agree with those of Reiset, showing that variations in the amount of carbonic acid only occur between very narrow limits and are due to local influences, and, in general, that the carbonic acid is uniformly distributed throughout the lower strata of the atmosphere. They have continued their investigations upon the subject, and have applied their method of analysis to the air of elevated regions. Additional interest is lent to this part of their work, from the fact that some recent investigations seem to indicate a decided diminution in the amount of carbonic acid in the air upon mountains. The method of analysis devised by them, and which has been found to be capable of giving extremely accurate results, consists essentially in drawing a measured volume of air through tubes filled with fragments of pumice-stone saturated with caustic potash. These tubes are sealed at both ends before the blowpipe, immediately at the close of each experiment, and the determination of the amount of carbonic acid absorbed may then be made in the laboratory after an indefinite time. The air was always drawn through metallic tubes from a distance of 8 to 10 metres to the windward side of the operator.

The point selected for carrying on the experiments was the summit of the Midi in the Pyrenees, at the altitude of 2877 metres

(9422 ft.) above the level of the sea. This is an isolated peak distant from any other elevated summit; the air circulating about it is generally that of the upper currents of the atmosphere; and the great velocity of the wind dismisses any suspicion of local influence. During the course of the experiments the direction of the wind and the state of the atmosphere varied frequently; nevertheless, the proportion of carbonic acid in the air was found to be constant, the mean of a large number of observations giving 2.86 parts by volume of carbonic acid to 10,000 parts of air. This agrees very closely with the figure found in the experiments upon the plain at Vincennes (2.85). For the sake of comparison, experiments were made in two valleys at the foot of the Pyrenees, one near Pierrefitte (altitude 507 m.) and the other near Luz (altitude 730 m.) At the first station the result obtained was 2.79 volumes of carbonic acid to 10,000 parts of air, and at the second 2.69, the latter determination being made in the midst of a luxuriant vegetation. All the results obtained agree closely with those found in the lower regions of the atmosphere, and also with those found by Reiset and by Schultze in very varied situations.

As a result of their investigations MM. Muntz and Aubin consider themselves justified in stating that carbonic acid is uniformly distributed throughout the atmosphere, and that their results confirm the statements made by Reiset upon the subject and the theories of Schloesing in reference to the circulation of carbonic acid upon the surface of the globe.—(*Comptes rendus*, 93, 797).

R. D. C.

Transformation of Xanthine into Theobromine and Caffeïne.

Xanthine is obtained from uric acid by reduction, is a constituent of certain rare urinary calculi, and can be prepared from guanine, a constituent of guano. It has the formula $C_5H_4N_4O_2$, while guanine has the formula $C_5H_5N_5O$. The formula of caffeïne, the alkaloid of coffee and tea, is $C_8H_{10}N_4O_2$. Caffeïne is the methyl derivative of theobromine, an alkaloid found in the chocolate bean. The formula of theobromine is hence $C_7H_8N_4O_2$. On comparing the formula of xanthine $C_5H_4N_4O_2$ with that of theobromine $C_7H_8N_4O_2$, it appears possible that the latter may be the dimethyl derivative of the former. Strecker made this suggestion some years ago, but, though he made some experiments with the object of determining whether the relation exists or not, they gave only negative results. EMIL FISCHER, in continuing his investigations on caffeïne, has again attempted to transform xanthine into theobromine, and has been successful. The lead salt of xanthine, which is a crystalline precipitate, was treated with methyl iodide in a sealed tube for twelve hours at 100°. Complete transformation was effected. The chief product had all the properties of theobromine.

The theobromine thus obtained was transformed into caffeïne by the usual method. It is thus shown that theobromine is dimethylxanthine; and that caffeïne is trimethylxanthine. Thus a direct line of connection is established between the active principles of guano and of coffee and tea.—(*Berichte der deutschen chemischen Gesellschaft*, 15, 453.) R. D. C.

On the Active Condition of Oxygen.

In an interesting article, MORITZ TRAUBE discusses the various opinions that have been advanced with reference to the remarkable change of oxygen from the ordinary passive condition to the active condition. He then, further, describes a number of experiments which he undertook with the object of determining whether, when hydrogen dioxide is formed in consequence of slow oxidation of metals in the presence of water and air, its formation is due to oxidation of water, as is commonly held, or to reduction of oxygen. He shows that in most cases the formation cannot be ascribed to an oxidation process; for experiment proves that, if substances which are easily oxidized are present, they are not oxidized under the circumstances which give rise to the formation of hydrogen dioxide. Thus, when zinc is shaken with water and air, hydrogen dioxide is formed; but if indigo-sulphuric acid, an easily oxidizable substance, is present in the water, it is not oxidized. Hence it is not probable that the water, which in general resists the action of oxidizing agents, is oxidized under these conditions. It is also shown that potassium nitrate is readily reduced when brought together with zinc, water, and air, hydrogen dioxide being formed at the same time. The action accompanying the formation of the dioxide is reduction; and, in all probability, the dioxide itself is formed by the addition of hydrogen directly to oxygen, and not by the addition of oxygen to water.

The remarks introductory to the paper are interesting and are here given: "Oxygen at the ordinary temperature is characterized by great passivity. While at high temperatures it burns up all organic substances without exception, at ordinary temperature it affects but very few of them. In the animal body, on the other hand, it becomes active, and now has the power of effecting oxidations at temperatures below 40° which it can otherwise effect only at red heat. Here it burns up all carbohydrates, fats, and albuminoids, forming carbon dioxide and water, the alkali salts of the plant acids forming alkali carbonates. Regarded from this standpoint, the adult animal, which neither loses nor gains in weight, plays the part of a catalytic body, which without suffering material change in composition, causes at low temperatures, by means of the oxygen of the air, the almost complete combustion of enormous quantities of food. But not only animal organisms have the power of rendering oxygen active; the same property, though to a much less extent, is possessed by plants, or, in general, by all organisms down to and including bacteria and fungi. There does not exist an organism which is indifferent towards oxygen; which, when brought in contact with this gas, will not take it up and be at least partly converted into carbon dioxide. Upon this power is based the most important act connected with the life process, the chemical part of respiration with which the effecting of the most important phenomena of life is intimately associated.

"It was formerly assumed, in accordance with Liebig's view, that respiration serves only the purpose of keeping up the temperature of the body and that the oxidation processes only take place in the blood. Even J. R. Meyer was of the opinion that respiration only produces heat which is transformed into motion in the muscles, and that the blood is the real hearth of the organic combustion processes. I first pointed out, with conclusive reasons, that the real hearth of the respiratory processes is, not the blood, but the tissues of the body, above all the muscles; that the oxygen taken up in the lungs is set free in the capillaries of the body, enters as dissolved gas into the tissues of the individual organs; and that in this way each individual organ breathes independently at the expense of the free oxygen. It is only in consequence of this breathing that the individual organs are enabled to grow, to perform their functions, to yield secretions, and to generate the different forces which characterize them, as, for example, the force of the muscle, nerve force, &c.

"Thus, not only do organisms as a whole have the power to make oxygen active, but each of their organs, indeed each individual cell; or rather they contain substances which have this power. Hence the problem of active oxygen is in the highest degree important, as well for physiology as for chemistry.

"Oxygen can also be made active by a few processes which take place without the organism. Thus, as is well known, it is affected in a high degree by platinum and phosphorus. In the presence of finely divided platinum it oxidizes energetically at the ordinary temperature hydrogen and alcohol, substances towards which it is usually indifferent. But, although the phenomena in inanimate nature are much more accessible to experimental investigation than the more complicated phenomena of life, a satisfactory theory of the process has not yet been framed on an experimental basis. A number of hypotheses regarding the process in inanimate nature as well as in the organisms have been advanced."

The views of De la Rive, Liebig, Schönbein, and Brodie are then given, and finally reference is made to the view of Hoppe-Seyler, according to which "hydrogen in the nascent state has the power to split the molecule of oxygen, uniting with one atom of the molecule and thus setting free the other as *active* oxygen possessed of highly energetic oxidizing power. According to the view of the same author the life process in the animal body resembles a case of decomposition accompanied by an evolution of hydrogen, and it is this nascent hydrogen which renders the oxygen taken up in respiration active."

He then speaks of an hypothesis advanced by himself in 1858. "According to this the oxygen is rendered active by *oxygen transferrers* (Sauerstoffüberträger). These are bodies which . . . have the power of giving up easily to other bodies the oxygen which they absorb and then again taking up oxygen immediately. This process may be followed readily when the oxygen transferrer is colored in oxidized condition and colorless when reduced.

"The ammoniacal solutions of copper salts, and indigo-carmine, are easily reduced by many bodies, as grape sugar, and then become colorless. If, however, they are in contact with oxygen, they take it up again and are changed back to their original condition, only to give it up to the sugar. This alternating reduction and oxidation continues until all the sugar is oxidized, while the oxygen transferrer itself (for example, the ammoniacal copper solution) appears unchanged at the end of the experiment. Thus small quantities of the transferrers can transform large quantities of bodies which of themselves can not take up oxygen. . . . In the different parts of the paper which are to appear these various hypotheses will be discussed in full."—(*Berichte der deutsch. chem. Gesell.* **15**, 659.)

Formation of Alloys by Pressure.

W. Spring has shown that, when a mixture of bismuth filings, cadmium and tin in the proportions necessary for the formation of Wood's alloy, is subjected to a pressure of 7500 atmospheres, the mass thus obtained powdered and again subjected to the same pressure, a metallic block is formed which has all the physical properties of the alloy. Its specific gravity, color, hardness, brittleness, and fracture are the same; and when thrown into water heated to 70°, it melts at once. In like manner Rose's metal was made by subjecting the proper mixture of lead, bismuth and tin to high pressure. If zinc and copper filings are repeatedly subjected to pressure, a mass resembling brass is finally obtained.—(*Berichte der deutsch. chem. Gesell.* **15**, 595.)

On the Conduct of Nitrogen Tetroxide towards Sulphuric Acid.

Lasne and Benker have recently taken out a patent in France for an invention having reference to the improvement of the processes involved in the manufacture of sulphuric acid. The improvement consists in introducing sulphurous acid and steam into the gases which enter the Gay-Lussac tower, so as to secure the reduction of all the nitrogen tetroxide N_2O_4, to the trioxide N_2O_3, and the formation of nitroxylsulphuric acid, $SO_2(OH)(ONO)$.

The object is to prevent loss of nitrogen in the form of the tetroxide. G. LUNGE now calls attention to the fact that the invention is based on a wrong conception of the conduct of nitrogen tetroxide towards sulphuric acid; that the tetroxide is readily and completely absorbed by sulphuric acid of 1.71 specific gravity, the weakest acid ever used in the Gay-Lussac tower; and that the acid acts upon the tetroxide, giving rise to the formation of nitroxylsulphuric acid and nitric acid, according to the equation:

$$N_2O_4 + SO_2(OH)_2 = SO_2(OH)ONO + NO_3H.$$

If, then, in the process of Lasne and Benker the introduction of sulphurous acid is of any value, the reason for this is certainly not what the inventors think it is. There is some doubt concerning the advantages of the process, as the statements of the manufacturers in regard to it are conflicting.—(*Berichte der deutsch. chem. Gesellschaft*, **15**, 488.)

The Atomic Weights of Lanthanum and Didymium.

The atomic weights of lanthanum and didymium have been redetermined by Brauner.[1] To lanthanum, without giving any details, he assigns the value 138.88. By converting didymium oxide into the sulphate, he found the following percentages of the former corresponding to the latter:

58.676
58.681
58.685

The mean is 58.681, for which the probable error is ±.0035.

If O = 16 and S = 32.074, this mean gives Di = 146.58.

If H = 1 and O = 15.96, this mean gives Di = 146.18.

In my recent recalculation of the atomic weights I found O = 15.9633, ±.0035, and S = 31.964, ±.012. Upon the basis of these values Brauner's data give Di = 146.210, ±.035.

It is worth while to compare Brauner's results with those of Cleve, which were obtained by the same method. Reckoned with $SO_3 = 80$, we have the following figures:

From Cleve's data . . .	Di = 147.021
From Brauner's data . . .	Di = 146.423
Difference,	0.598

It is plain that additional determinations are still needed.

F. W. CLARKE.

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[1] Ber. d. deutsch. chem. Gesell. **15**, 109.

Vol. IV. [May, 1882.] No. 2.

AMERICAN
CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Harvard College.

XVII.—ON CERTAIN SUBSTANCES OBTAINED FROM TURMERIC.

I.—CURCUMIN.[1]

By C. Loring Jackson and A. E Menke.

The chemical study of curcumin, the yellow coloring matter of turmeric, dates from a paper[2] by A. Vogel, Sr., and Pelletier, published in 1815, although even before this turmeric-paper had been used as a test for alkalies, and its action with boric acid and various salts observed.[3] No analysis is given in this paper, and the low melting-point (40°) and description of the method of preparation show that the "yellow coloring-matter of turmeric" obtained by Vogel and Pelletier was principally composed of resin and turmeric oil; they proved, however, that it contained no nitrogen, and studied its action with alkalies, acids, and certain salts, especially acetate of lead.

In 1842 A. Vogel, Jr.,[4] analysed a similar but perhaps somewhat purer preparation, which, however, must have consisted in great part of the yellow resin contained in the root, as it also melted at 40°; it is not wonderful, therefore, that his analyses led to no formula.

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[1] From the Proceedings of the American Academy. Communicated by the authors.

[2] Journal de Pharmacie **1**, 289.

[3] Trommsdorff, Trommsdorff's Journal von Pharm. **16**, 96. Sementini, Bibliothèque Britannique, Jan. 1815.

[4] Journ. de Pharm. et de Chim. sér. 3, **2**, 20.

Passing over a number of unimportant notices,[1] we come next to a paper by Schlumberger,[2] in which the action of a mixture of sulphuric and boric acids on crude curcumin is studied, and a description given of the product called by him rosocyanin, because it dissolved in alcohol with a fine red color, and was turned blue by alkalies. He also describes a resinous product of the action of boric acid on curcumin (pseudocurcumin).

Two years later, in 1868, Bolley, Suida, and Lange[3] examined the turmeric oil, and published a new analysis of a purer curcumin (melting-point 120°); but it was not till 1870 that curcumin was obtained essentially pure. In this year Daube,[4] Ivanow-Gajewsky,[5] and Kachler[6] published independent papers on the subject, of which Ivanow-Gajewsky's is entitled to the precedence, as the number of the Berlin Berichte which contained Daube's original paper gave a notice in the Correspondence of the reading of Gajewsky's paper before the Russian Chemical Society a month earlier. In addition to an analysis of the turmeric oil, he assigns, as the simplest possible, the formula C_4H_4O to curcumin, which after crystallization from ether or benzin melted at 172°. Daube, on the other hand, after extracting his curcumin with benzol, and purifying it by conversion into the lead salt, obtained the melting-point 165°, and the formula $C_{10}H_{10}O_3$. He also found that it was decolorized by sodium amalgam and alcohol, and converted into oxalic acid by dilute nitric acid.

Kachler, who did not succeed in crystallizing his curcumin, although both Ivanow-Gajewsky and Daube got crystals, obtained the same formula as the former, that is, C_4H_4O, or some multiple of it. He also studied the action of sodium amalgam upon it, and that of hot zinc dust, but with no very definite results in either case; whereas by fusing curcumin with potassic hydrate, he obtained protocatechuic acid. From the turmeric oil he obtained essentially the same analytical results as Ivanow-Gajewsky.

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[1] Desfosses, Ann. Chim. Phys. **16**, 76; A. Vogel, Jr., Répert. Pharm. sér. 3, **3**, 178; H. Rose, Pogg. Ann. **102**, 545; Lepage, Archiv der Pharm. Ser. 2, **97**, 240; Leube, Vierteljahrsschr. pr. Pharm. **9**, 395; Alex. Müller, J. pr. Chem. **80**, 119; Wittstein, Vierteljahrsschr. pr. Pharm. **9**, 282; Schutzenberger, Paraf. Mul. Soc. Bull. 1861, 503; Ludwig, Archiv der Pharm. **106**, 169; Kraut, Zeitschr. anal. Chem. **4**, 168.

[2] Bull. Soc. Chim. sér. 2, **5**, 194.

[3] J. pr. Chem. **103**, 474.

[4] Berichte der deutschen chemischen Gesellschaft, **3**, 609.

[5] *Ibid.* **3**, 624.

[6] *Ibid.* **3**, 713.

In 1872 Ivanow-Gajewsky published a second paper[1] on turmeric, containing another method for extracting curcumin, which, however, gave it a melting-point of 140°, and an analysis of the lead salt supporting his formula $C_{16}H_{16}O_4$ ($=(C_4H_4O)_4$). Moreover he confirmed the results of Kachler with fusing potassic hydrate (protocatechuic acid) and zinc dust, and states that the oil obtained with the latter is identical with turmeric oil, of which a new analysis is given, and its oxidation (yielding valeric and caproic acids) and action with phosphoric pentachloride studied. He also prepared and analysed rosocyanin, but was unable to find a satisfactory formula for it.

Finally, in 1873, he published the last paper[2] we have been able to find on this subject, in which he states that curcumin yields on oxidation with potassic dichromate terephthalic acid, and that rosocyanin contains no boron, and, fused with potassic hydrate, yields paraoxybenzoic acid.

In brief, the following facts had been established in regard to curcumin at the time that we began our research upon it:—Its formula was either $C_{10}H_{10}O_3$ or $C_{16}H_{16}O_4$; the highest melting-point observed was 172°; with alkalies it formed reddish-brown salts; with boric and sulphuric acids rosocyanin; it was susceptible of reduction, and gave an oil with zinc dust; by oxidation it yielded oxalic acid or terephthalic acid, and by fusion with caustic potash protocatechuic acid.

Accordingly we first turned our attention to the determination of its formula.

Extraction and Purification of Curcumin.

After several experiments we have adopted the following method as the best and most convenient:—The turmeric oil is first removed from the ground root by treatment with ligroine;[3] then the curcumin, mixed with a large quantity of resin, is extracted with ether, and finally purified by crystallization from alcohol.

The turmeric used by us has been principally Bengal turmeric, bought of Messrs. E. and F. King, of Boston; we have, however, also extracted enough of the Madras turmeric, the only other brand occurring in the Boston market, to assure ourselves of the identity of the curcumin obtained from both.

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[1] Berichte der deutschen chemischen Gesellschaft, **5**, 1103.

[2] *Ibid.* **6**, 196.

[3] In our first experiments we followed Ivanow-Gajewsky, and used carbonic disulphide for this purpose; but we have found that ligroine is not only much cheaper and more agreeable to work with, but yields a purer oil.

For a full description and history of turmeric, which consists of the root-stocks of the *Curcuma longa*, a plant of the ginger family, growing in India and other parts of the East, we would refer to Flückiger and Hanbury's Pharmacographia,[1] and to a full botanical article recently published by A. Meyer[2] in the Archiv der Pharmacie.

The extracter was of the form recently described by Scheibler,[3] as this was the only one of which we have found a description adapted to the thorough extraction of large quantities of material; those forms in which the drug is not kept covered with the extracting liquid being apt to leave the edges partially unacted on. The only modification of Scheibler's apparatus made by us consisted in substituting a cylindrical tin vessel capable of holding 10 kil. of ground turmeric for the smaller glass vessel used by him. With a cooler 78 cm. long, the inner tube of which was a flattened U, also made of tin, the thorough extraction of the 10 kil. of turmeric could be accomplished in little more than a fortnight. The solvent was removed, after it had ceased to act, by forcing out as much as possible of it by air pressure, and then distilling off the rest by filling with steam a jacket which surrounded the vessel containing the turmeric.

The ligroine extract yielded on evaporation a dark yellow oil, amounting on the average to eleven per cent. of the weight of the root. The investigation of this substance will be described in a later paper.

The ether extract, a reddish-brown mass, varying in consistency from semi-liquid to solid according to the period of the extraction at which it was obtained, was treated with successive small quantities of cold alcohol, which dissolved the viscous impurities more easily than the curcumin. In very obstinate cases washing with ether was found advantageous; if, on the other hand, the extract was comparatively free from resin, it could be washed with alcohol upon a filter. In either case the residue was purified by recrystallization from alcohol until it showed the constant melting-point 178°.

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[1] Macmillan and Co., London, 1879.

[2] Arch. Pharm. Ser. 3, **18**, 401.

[3] Berichte der deutschen chemischen Gesellschaft, **13**, 338.

The average yield of curcumin was 0.3 of one per cent.; this, however, is only the amount that can be extracted by the process just described; the quantity contained in the root is much larger, as a considerable amount remained mixed with the resinous impurities, and the green fluorescence of the crude turmeric oil pointed to the presence of some curcumin in this substance.

Composition of Curcumin.

The following combustions were made of the curcumin purified as just described and dried at 100°. In most of these analyses a slight ash was left, the amount of which has been subtracted from the weight of substance before calculating the percentages.

I. 0.1106 gram of substance gave 0.2774 gram of CO_2 and 0.0563 gram of H_2O. No ash.

II. 0.2180 gram gave 0.5450 gram of CO_2 and 0.1099 gram of H_2O. Ash 0.0007 gram.

III. 0.2149 gram gave 0.5376 gram of CO_2 and 0.1090 gram of H_2O. Ash 0.0006 gram.

IV. 0.2195 gram gave 0.5480 gram of CO_2 and 0.1099 gram of H_2O. Ash 0.0006 gram.

V. 0.2743 gram gave 0.6815 gram of CO_2 and 0.1378 gram of H_2O. Ash 0.0010 gram.

	I.	II.	III.	IV.	V.	Mean.
Carbon	68.43	68.39[1]	68.42[1]	68.27[1]	68.00	30
Hydrogen	5.65	5.62	5.69	5.59	5.60	5.63

All these analyses were made with curcumin from Bengal turmeric: I. and II. of different portions of the same sample, III., IV., and V. of different samples.

The following analysis was made of curcumin extracted from Madras turmeric:

0.3467 gram gave 0.8612 gram of CO_2 and 0.1870 gram of H_2O. No ash.

Carbon	67.74
Hydrogen	5.99

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[1] These numbers become, if the ash is not subtracted from the weight of the substance:

	II.	III.	IV.	V.
Carbon	68.17	68.23	68.09	67.75
Hydrogen	5.60	5.64	5.56	5.58

The sample analysed was very red, and the somewhat lower percentage of carbon obtained was undoubtedly due to the presence of an impurity which causes the curcumin to crystallize in red burrs, as is shown by the following analysis of a very red sample of Bengal curcumin:

0.2168 gram of substance gave 0.5400 gram of CO_2 and 0.1057 gram of H_2O. No ash.

Carbon	67.93
Hydrogen	5.42

It is to be observed, however, that enough of this impurity to change the crystalline habit and color of the curcumin has but a very slight effect on the percentage composition, and, it may be added, does not lower the melting point more than one degree. That it is formed by the oxidation of curcumin by the action of the air, appears from the fact that pure yellow curcumin was partially converted into red burrs when moistened with alcohol and exposed to the air for a long time. When once formed, the impurity can be removed only by repeated crystallization, and the amount of Madras curcumin at our disposal did not admit of this, nor did we take the trouble to prepare a larger supply, as the above analysis with the melting point 178° is sufficient to establish the identity of the Madras and Bengal curcumins.

The following comparison shows that our results agree tolerably well with those of Daube, but are entirely at variance with those of Kachler and Ivanow-Gajewsky. (As no analyses are given in the abstract of the latter's article, which alone is at our disposal, we have given the theory for his formula, $C_{16}H_{16}O_4$, under his name.)

	Ivanow-Gajewsky.	Kachler.			Daube.		Jackson and Menke Mean.
Carbon	70.58	69.90	69.87	67.90	67.89	67.92	68.30
Hydrogen	5.90	5.70	5.59	5.66	5.76	5.70	5.63

There are, then, eight analyses of curcumin which support a percentage of carbon in the neighborhood of 68, against three (or more) in favor of one near 70.[1]

It is probable that the high results obtained by Ivanow-Gajewsky and Kachler were due to the presence of resinous impurities, since their predecessors, who analysed exceedingly impure curcumin, as shown by the low melting point, obtained the following results:

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[1] Ivanow-Gajewsky obtained a percentage of lead in a plumbic salt agreeing with his combustion; but this result is more than counterbalanced by the analyses of derivatives of curcumin given later in this paper.

	A. Vogel, Jr.	Bolley, Suida and Lange.
Carbon	69.50	69.07
Hydrogen	7.46	6.40

This view is further supported by the fact that we obtained a higher melting point, 178°, than any one else; Daube found 165°, Ivanow-Gajewsky 172°, later 140°, while Kachler gives no melting point, and did not succeed in obtaining his curcumin crystallized. In view of these facts we feel no hesitation in rejecting all the previous analytical results except those of Daube.

Daube gives curcumin the formula $C_{10}H_{10}O_3$, but our results, and for that matter his, agree much better with the formula $C_{14}H_{14}O_4$, as appears from the following comparison:

	$C_{10}H_{10}O_3$	$C_{14}H_{14}O_4$	Daube.	Jackson and Menke.
Carbon	67.42	68.29	67.90	68.30
Hydrogen	5.62	5.69	5.70	5.63

We have therefore adopted the formula $C_{14}H_{14}O_4$, which is also confirmed by the analyses of derivatives of curcumin to be given later in the paper.

Properties of Curcumin.

Curcumin crystallizes from alcohol in stout needles, which under the microscope appear as well-formed prisms with square ends, or spindle-shaped crystals, often arranged in radiating groups; in color it is orange to yellow, according to the size of the crystals, with a beautiful blue reflex; its solution in ether exhibits a very strong green fluorescence; when pure it has no odor; it melts at 178°, apparently with decomposition.[1] It is nearly insoluble in water, somewhat soluble in cold, more readily in hot alcohol and methyl alcohol, more soluble in glacial acetic acid than in alcohol, less so in ether, very slightly soluble in benzol[2] and carbonic disulphide, and essentially insoluble in ligroine. Strong sulphuric acid dissolves it with a fine reddish-purple color, which changes to black from charring after some time; strong hydrochloric acid produces the same effect, but with more difficulty. It is readily soluble in alkalies and alkaline carbonates, and is even dissolved to a slight extent when boiled with precipitated calcic carbonate and water. The solution in ammonic hydrate loses ammonia when boiled, and deposits unaltered curcumin. A solution of baric hydrate converts it into a blackish-red powder, but lime-water gives a red solution like that obtained from calcic carbonate. It is not affected by acid sodic sulphite.

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[1] Daube found 164°; Gajewsky, 172° or 140°.

[2] Compare Daube, Berichte der deutschen chemischen Gesellschaft, 3, 609.

Salts of Curcumin.

In taking up the study of this subject we were at first attracted to the lead salt by the analyses and descriptions of Ivanow-Gajewsky and Daube; but, after several experiments, we decided that it was too indefinite a substance to throw much light upon the nature of curcumin, and accordingly turned our attention to the potassium salts, which at first did not seem promising, but on proper treatment have yielded satisfactory results. Before describing these, however, we will say, that there seem to be at least two lead salts, as we have obtained a dark claret precipitate and also a flame-colored one. The most promising method of preparation seemed to be boiling curcumin with precipitated calcic carbonate and water, and adding plumbic acetate to the filtrate; in this way the flame-colored salt was obtained.

We have succeeded in obtaining two potassium salts, containing one and two atoms of potassium respectively.

Dipotassic Salt of Curcumin $K_2C_{14}H_{12}O_4$.

This was made by adding a large excess of a strong alcoholic solution of potassic hydrate to a hot saturated solution of curcumin in alcohol; if the solutions are strong enough, flame-colored crystals of the salt are deposited on cooling; if this is not the case, it can be precipitated by addition of ether. If an insufficient amount of potassic hydrate is used, a dark red solution of the monopotassic salt is formed, which becomes lighter on the addition of more potassic hydrate as the second atom of potassium is taken up. The salt was crystallized from boiling alcohol to which a few drops of ether had been added, washed with a mixture of alcohol and ether, then with ether alone, pressed on filter-paper, and dried as rapidly as possible in a steam-drying closet containing some potassic hydrate.

0.7168 gram of the salt gave, heated with sulphuric acid, 0.3824 gram of K_2SO_4.

0.2675 gram gave 0.1459 gram of K_2SO_4.

	Calculated for $C_{14}H_{12}K_2O_4$	Found.	
Potassium	24.27	23.95	24.48

If curcumin had the formula $C_{16}H_{16}O_4$ the dipotassic salt would contain—

Potassium 22.46.

The salt consists when first formed of flame-colored needles in globular radiating groups, but becomes deep claret on drying. It is freely soluble in water, not quite so soluble in alcohol, and essentially insoluble in ether; the alcoholic solution takes on a magenta color when exposed to the air, and the salt seems to absorb carbonic dioxide readily, although the change of color was more probably due to oxidation.

Monopotassic Salt of Curcumin $KC_{14}H_{13}O_4$.

If an excess of potassic carbonate is added to a hot solution of curcumin in absolute alcohol, there is a violent effervescence, and the liquid turns deep blood red. After slight concentration the excess of potassic carbonate was removed by filtration, the salt precipitated with ether, and purified by washing with ether. An attempt to crystallize it from a mixture of alcohol and ether gave no satisfactory result. Pressed between filter-paper, and then dried at 100°, it gave the following results:

I. 0.4808 gram of the salt gave after ignition with sulphuric acid 0.1540 gram of K_2SO_4.

II. 0.5381 gram of salt gave 0.1680 gram of K_2SO_4.

	Calculated for $KC_{14}H_{13}O_4$	Found. I.	Found. II.
Potassium	13.76	14.36	14.02

$KC_{16}H_{15}O_4$ contains 12.60 per cent. of potassium.

This salt is precipitated in crimson black flocks, which dry to a mass having the green color and lustre of rosanilin, although the shade is somewhat blacker. It is very easily soluble in water and alcohol, giving blood-red solutions, but insoluble in ether, and does not seem to be altered by exposure to the air. It can also be made by the action of an excess of curcumin on the dipotassic salt, or by adding potassic hydrate not in excess to curcumin suspended in alcohol. It is very much more soluble than the dipotassic salt.

Curcumin forms also a flame-colored calcium salt, slightly soluble in water, which can be made by adding calcic chloride to a solution of the monopotassic salt. The same salt is formed in small quantity when calcic carbonate is boiled with curcumin and water or alcohol, carbonic dioxide being set free.

The zincic salt seems to be soluble, the baric salt insoluble,[1] while the silver salt is probably very unstable, as curcumin is decomposed when boiled for more than a minute with argentic nitrate and alcohol.

The fact that only one atom of the hydrogen contained in curcumin can be replaced by the potassium of potassic carbonate would point to the existence of one, and only one, carboxyl group in its molecule; the presence of this group is confirmed farther by the power of decomposing calcic carbonate possessed by curcumin.[2] The replacement of a second atom of hydrogen when curcumin is treated with potassic hydrate in excess indicates the existence of a hydroxyl group, probably a phenol hydroxyl, and it would seem, therefore, that curcumin is a diatomic monobasic acid.

Esters of Curcumin.

Although the analyses of the potassium salts had agreed with the formula of curcumin derived from the analysis of the original substance, it seemed desirable to confirm this formula still farther by the study of some derivative of curcumin more stable and easily handled than the salts; we accordingly took up the investigation of the esters, but found that the ethyl ester made by the action of ethyliodide on the dipotassic salt was a disagreeable brownish-black tarry substance, that could not be obtained in a crystalline condition. We therefore abandoned the study of this substance and turned our attention to the monoparabrombenzyl ester, which we preferred to the benzyl ester, in the first place because of the great tendency of the parabrombenzyl compounds to crystallize, and secondly, since the presence of bromine increased the difference between the percentages of carbon in the two formulas by more than five-tenths of one per cent., and also gave a third element whose quantity could be determined.

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[1] As our work on the potassium salts had achieved the end for which we undertook the study of the salts of curcumin, we thought it not worth while to purify any of the other salts for analysis.

[2] Some experiments on the action of phosphorus trichloride upon monoethylcurcumin confirmed the presence of a carboxyl group, so far as they went, but the product was too ill-defined to repay a thorough study.

Monoparabrombenzyl Ester of Curcumin $C_{14}H_{13}(C_7H_6Br)O_4$.

To an alcoholic solution of the monopotassic salt of curcumin an excess of parabrombenzylbromide was added, and the mixture allowed to stand for several days, when it was found that pale yellow crystals mixed with potassic bromide had been deposited; the dark-colored liquid was poured off, and the solid residue freed from parabrombenzylbromide by repeated treatment with hot ligroine, and from curcumin by boiling with successive portions of aqueous potassic carbonate, until it ceased to give a red solution. The essentially pure ester thus obtained was boiled several times with alcohol, which dissolved a small portion of it, while the residue melted to a reddish-black tar; upon dissolving this in glacial acetic acid and precipitating with water, yellowish flocks were thrown down, the melting point of which was compared with that of the similarly-colored indistinct crystals obtained by cooling the alcoholic extract. As both these substances melted, or, more accurately, drew together, at the same temperature, the ester seemed to be essentially pure, and after drying at 50°-60° was analysed.

I. 0.1796 gram of substance gave 0.3980 gram of CO_2 and 0.0817 gram of H_2O.

II. 0.2506 gram of substance gave according to Carius 0.1156 gram of AgBr.

	Found.	Calculated for	
		$C_{14}H_{13}(C_7H_6Br)O_4$	$C_{16}H_{15}(C_7H_6Br)O_4$
Carbon	60.43	60.72	62.58
Hydrogen	5.05	4.57	4.76
Bromine	19.63	19.26	18.14

From these results there can be no doubt that $C_{14}H_{14}O_4$ is the true formula of curcumin.

The ester consists of indistinct crystals, grouped in forms like cauliflowers, of a much paler yellow color than curcumin; it melts at 76°–78°, beginning to draw together at 76°, and becoming thoroughly liquid at 78°; we have not succeeded in obtaining it with a perfectly sharp melting-point. It is more soluble in glacial acetic acid than in alcohol, nevertheless the latter is to be preferred as a solvent for obtaining crystals, since the substance is apt to separate from the hot glacial acetic acid in a fused tarry condition. It is readily soluble in ether and benzol, but does not crystallize well from these solvents; slightly soluble in carbonic disulphide; essentially insoluble in ligroine; not attacked by a solution of potassic carbonate, but soluble in potassic hydrate, although without the red color charcteristic of curcumin. As the analysis of this ester establishes our formula, we have not continued the study of the esters.

Oxidation of Curcumin.

Our experiments on this subject can be divided into two classes, those in which we made a complete oxidation of the substance, and those in which a partial oxidation was obtained by using an insufficient amount of the oxidizing agent, or one less energetic.

Complete Oxidation.—As Ivanow-Gajewsky states that he obtained terephthalic acid by the action of potassic dichromate and sulphuric acid on curcumin, we turned our attention first to this experiment. Unfortunately only an abstract of his paper is accessible to us, so that we could not find the exact conditions of his oxidation; we have therefore varied the conditions in several ways, but always with the same result. It will be sufficient to describe a single experiment. Half a gram of curcumin was mixed with sulphuric acid previously diluted with its own volume of water, and solid potassic dichromate added; the action was extremely violent, accompanied by great evolution of heat and strong effervescence; the gas given off was carbonic dioxide. At the end of the process there was no insoluble substance in the liquid, which was therefore distilled until it was reduced to a small volume. The strongly acid distillate, treated with argentic oxide, after filtering and concentration, deposited long flattened needles, which looked exactly like argentic acetate, and were proved to consist of this substance by the following silver determination:

0.1812 gram of salt dried at 100° gave 0.1559 gram of AgCl.

	Calculated for $AgC_2H_3O_2$	Found.
Silver	64.68	64.76

There was no other volatile acid in the distillate, and no organic matter could be found in the residue from the distillation. If the action was moderated by using more dilute sulphuric acid, the phenomena were the same, except that it was necessary to start the reaction by the aid of heat. In none of the products of the oxidation of curcumin with potassic dichromate could any terephthalic acid be found, they consisted only of acetic acid and carbonic dioxide.

If curcumin is dropped into fuming nitric acid it dissolves with a hissing noise and formation of nitrous fumes and hydrocyanic acid. The red liquid thus obtained gave no precipitate with water; on evaporation it deposited brownish crystals, principally oxalic acid, but it was not further examined. In this respect we confirm the results of Daube, who also obtained oxalic acid from curcumin and nitric acid.

Incomplete Oxidation.—When curcumin was dissolved in aqueous potassic hydrate, a solution of potassic permanganate added, not in excess, and after the oxidation had ceased, the liquid acidified with sulphuric acid, a strong smell of vanilla was observed. The liquid was accordingly filtered, and the precipitate thoroughly washed with boiling water, the filtrate and wash-water extracted with ether, and the extract treated with acid sodic sulphite, as directed by Tiemann and Haarmann.[1] The product was an oil, having a strong smell of vanilla and gradually solidifying in circular groups of radiating needles; the amount, however, was extremely small, and none of this product was obtained with an excess of potassic permanganate or when the quantity of curcumin was much more than half a gram. The same substance was obtained with various weak oxidizing agents, such as bleaching powder and water, potassic ferricyanide with potassic hydrate, and even the action of atmospheric oxygen on curcumin dissolved in potassic hydrate. Of these the mixture of potassic hydrate and potassic ferricyanide gave the best yield, but even this was extremely small—in fact, after uniting the product from all the oxidations made by us, in which over eight grams of curcumin were used, the quantity was not enough for complete purification. By sublimation, however, and subsequent crystallization from boiling water, it was obtained in white needles resembling in appearance and odor the vanillin from the vanilla-bean and melting at 79°. Vanillin melts at 80°–81°.

In addition to the vanillin there were formed carbonic dioxide, a black amorphous substance with feebly acid properties, perhaps the aldehyd resin of vanillin, as it appeared in largest quantity when no vanillin was obtained, and an acid volatile with steam. We have not as yet made any complete study of these secondary products, because the properties of the humus-like substance are far from inviting, and the amount of the volatile acid is so minute that its isolation in quantity sufficient for analysis would be extremely laborious. We shall, however, return to these substances if we fail in finding easier methods for studying the nature of the side-chain.

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[1] Berichte der chemischen Gesellschaft, **8**, 1115.

As the small yield of vanillin was undoubtedly due to the presence of the phenol hydroxyl, which offered a point of attack for the oxidizing mixture, we next tried to increase our yield by replacing the hydroxyl hydrogen with some radical which would protect it from oxidation, and in this way not only prove that the substance was really vanillin, but also that it was one of the principal products of the oxidation. For this purpose we first tried to make acetylcurcumin by treating curcumin with acetylchloride; this gave a deep bluish-green liquid, which on standing turned brown, and then yielded on addition of water a yellowish precipitate which could not be obtained in crystals, its solutions forming on evaporation a dark-colored varnish. With acetic anhydride no better results were obtained, and as there seemed no prospect of getting a good analysis of the substance, it was at once oxidized with potassic permanganate. The result was not essentially better than that obtained with pure curcumin, and we accordingly turned our attention to the oxidation of diethylcurcumin, which was made by boiling the dipotassic salt with absolute alcohol and a slight excess of ethyliodide for six hours in a flask with a return cooler. On distilling off part of the alcohol and allowing the rest to evaporate spontaneously, the compound is left as a most uninviting brownish-black tar, which when heated with sodic hydrate dissolves with a dark red color resembling that of the alkaline solution of curcumin. Upon treating this solution with potassic permanganate until it was decolorized, filtering from manganic hydrate, and acidifying with sulphuric acid, a yellowish precipitate was obtained, which after two crystallizations from boiling water with bone-black melted at 195°, the melting point given by Wassermann[1] for ethylvanillic acid (Tiemann[2] gives 193°–194°).

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[1] Annalen der Chemie, **179**, 366.

[2] Berichte der deutschen chemischen Gesellschaft, **8**, 1127.

The nature of the substance was still further confirmed by the following combustion:

0.1216 gram of substance gave 0.2714 gram of CO_2 and 0.0707 gram of H_2O.

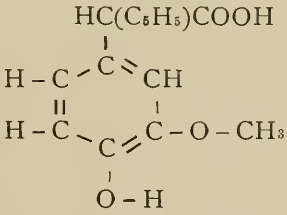
	Calculated for $C_{10}H_{12}O_4$	Found.
Carbon	61.22	60.87
Hydrogen	6.12	6.46

There can be no doubt, therefore, that the substance is ethylvanillic acid, and it was formed in such quantity that it must be considered one of the principal products of the reaction. If the potassic permanganate was not added in excess, and the liquid extracted with ether, crystals of ethylvanillin were obtained, which on sublimation formed an oil solidifying after a short time in large twinned crystals like those of cassiterite, and having a smell similar to that of vanillin, but not identical with it.

Summary of Results.

The formula of curcumin is $C_{14}H_{14}O_4$, as proved by analyses of curcumin itself, of its potassium salts, and its parabrombenzyl ester.

It is a phenol-carboxylic acid, as shown by the study of its salts. The presence of carboxyl is indicated by its power of driving carbonic acid out of potassic and calcic carbonates, and by the decomposition of its diethylester on boiling with potassic hydrate. It contains the vanillin group, and therefore its formula, as far as we have determined it, is:



We are at present engaged in the study of the group C_5H_5, and propose to extend our investigations to rosocyanin and the turmeric oil.

XVIII.—DIBROMIODACRYLIC AND CHLORBROMIODACRYLIC ACIDS.[1]

By Charles F. Mabery and Rachel Lloyd.

From the ease with which various substituted acrylic acids have been obtained from brompropiolic acid,[2] we were led to believe that derivatives of some interest would result by the simultaneous addition of different halogens. This idea was confirmed by a few preliminary experiments, which showed that iodine monobromide and iodine monochloride could readily be made to form addition-products with brompropiolic acid. These substances have been submitted to a careful study, and the results we have obtained are presented in this paper.

Dibromiodacrylic Acid.

Dibromiodacrylic acid was made from brompropiolic acid, by the action of iodine monobromide. In the preparation of iodine monobromide according to the method of Lagermarck,[3] the required weight of iodine, with an excess of bromine, was heated to 50° for ten minutes on the water-bath. Dibromiodacrylic acid was formed in small quantity, when the solid residue left by evaporation of the excess of bromine was dissolved in ether and allowed to stand with brompropiolic acid. The product of this reaction, however, consisted to a large extent of an oil, from which very little pure substance could be recovered. This difficulty was partially overcome by the application of heat; and by boiling the solution for an hour on the water-bath we succeeded in obtaining about forty per cent. of the amount theoretically required. The thick pasty mass left after the evaporation of the ether soon solidified, and was easily purified by crystallization from hot water.

Dibromiodacrylic acid dissolves readily in ether, alcohol, carbonic disulphide and chloroform. In cold water it is rather sparingly soluble; from a concentrated hot solution it falls at first as an oil, which crystallizes as the solution cools, in oblique prisms of the monoclinic system. It melts at 139°–140°, and sublimes slowly at higher temperatures.

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[1] The investigations described in the following papers were made under my supervision, and they formed a part of the work in the Summer Course of Instruction in Chemistry for 1881.—C. F. Mabery.

[2] Proceedings American Academy, **16**, 211, 235.

[3] Berichte der deutschen chemischen Gesellschaft, **7**, 907.

The composition of this substance was determined by the following analyses:

I. 1.0762 gram of the substance gave 0.3385 gram CO_2 and 0.0420 gram H_2O.

II. 0.1993 gram of the substance gave by the method of Carius 0.3385 gram $AgBr + AgI$.

	Calculated for $C_3HBr_2IO_2$.	Found.	
		I.	II.
C	10.11	9.85	...
H	.28	.43	...
2Br+I	80.63		80.21

To determine the solubility of this acid at ordinary temperatures, we used the method of V. Meyer. The filtered solution was neutralized with baric carbonate, and the barium estimated by precipitation with sulphuric acid.

I. 8.7164 grams solution gave 0.0968 gram $BaSO_4$.

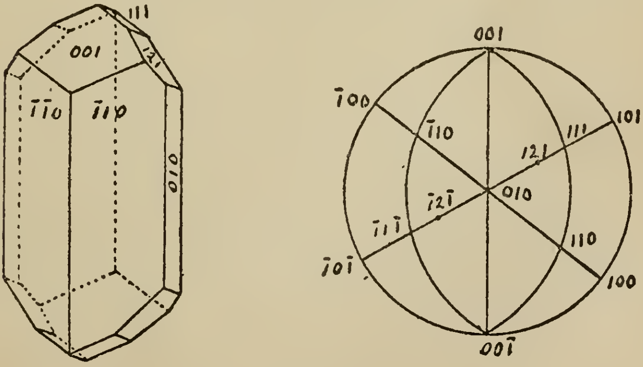
II. 9.7772 grams solution gave 0.1089 gram $BaSO_4$.

The solution saturated at 20° contains, therefore, the percentages:

I.	II.
3.39	3.40

Dr. W. H. Melville has made a crystallographic examination of this substance, and obtained the following results:

Crystalline Form of Dibromiodacrylic Acid.



MONOCLINIC SYSTEM.

Forms [001], [010], [110], [121], [111].[1]

Elements:—Clinodiagonal, $a = 0.617$
Orthodiagonal, $b = 1.$
Vertical Axis, $c = 0.581$
Angle of Axes = 52° 11½′

Angles between normals			Observed.	Calculated.
001	and	110	123° 26′	Fundamental angles.
110	"	010	64°	
111	"	110	59° 14½′	
111	"	010	62° 11′	61° 47′
121	"	010	42° 59′	42° 58′
121	"	001	70° 29′	70° 19′
121	"	110	55° 59′	56° 13′
121	"	$\bar{1}10$	84° 55′	85° 5½′

The following salts of this acid have been examined:

Baric dibromiodacrylate $Ba(C_3Br_2IO_2)_2.3\frac{1}{2}H_2O$.

To prepare the barium salt, a solution of the acid was neutralized with baric carbonate and the filtered solution concentrated by evaporation. On cooling the salt crystallized in rhombic prisms, which were very soluble in hot, less soluble in cold water. The air-dried salt lost three and a half molecules of crystal water at 80°.

I. 0.7087 gram of the air-dried salt lost 0.0512 gram H_2O at 80°.
II. 0.7273 gram of the salt lost 0.0535 gram H_2O at 80°.
III. 0.6244 gram of the salt lost 0.0441 gram H_2O at 80°.
IV. 0.6575 gram of the anhydrous salt gave 0.1808 gram $BaSO_4$.

	Calculated for $Ba(C_3Br_2IO_2)_2.3\frac{1}{2}H_2O$.	Found.		
		I.	II.	III.
H_2O	6.92	7.23	7.36	7.06

	Calculated for $Ba(C_3Br_2IO_2)_2$.	Found.
Ba	16.17	16.16

The solubility of this salt in cold water was determined by V. Meyer's method. The saturated solution was filtered, evaporated to dryness, and the barium estimated by ignition with sulphuric acid.

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[1] The form [111] appeared only on a few crystals.

I. 2.6342 grams of a solution saturated at 20° gave 0.1038 gram $BaSO_4$.

II. 2.0175 grams of a solution saturated at 20° gave 0.0806 gram $BaSO_4$.

From these determinations the following percentages were calculated:

I.	II.
14.32	14.52

Calcic dibromiodacrylate $Ca(C_3Br_2IO_2)_2$.

The calcium salt was made by saturating an aqueous solution of the acid with calcic carbonate. From the concentrated solution the salt crystallized in clustered needles which were less soluble in cold than in hot water. When air-dried it was constant at 80°.

0.4118 gram of the salt dried at 80° gave 0.0714 gram $CaSO_4$.

	Calculated for $Ca(C_3Br_2IO_2)_2$.	Found.
Ca	5.33	5.10

Potassic dibromiodacrylate $KC_3Br_2IO_2$?

This salt was prepared by neutralizing an aqueous solution of the acid with potassic carbonate and evaporating on the water-bath. It separated in the form of rhombic plates, which proved to be so deliquescent that we were unable to determine the water of crystallization.

0.8834 gram of the salt dried at 80° gave 0.1842 gram K_2SO_4.

	Calculated for $KC_3Br_2IO_2$.	Found.
K	9.92	9.92

Argentic dibromiodacrylate $AgC_3Br_2IO_2$.

From a hot aqueous solution of the acid the silver salt is precipitated by the addition of argentic nitrate in hexagonal plates. It may be recrystallized from hot water without decomposition, and it is but slightly affected by the action of light. The salt was dried over sulphuric acid for analysis.

1.0737 gram of the salt gave by precipitation with HBr 0.4288 gram AgBr.

	Calculated for $AgC_3Br_2IO_2$.	Found.
Ag	23.32	22.98

When dibromiodacrylic acid is heated to 100° in a closed tube with bromine, iodine is set free and bromine takes its place. The substance thus formed is identical with the tribromacrylic acid described by Professor H. B. Hill and one of us[1] as shown by its melting point 115°–118°, and by a study of its crystalline form. The following angles were measured by Dr. Melville:

	Angles between normals.	Tribromacrylic acid from dibromiodacrylic.	Tribromacrylic acid from brompropiolic.
Zone [010, 110]	110 and 010	65° 33′	65° 38′
	010 " $\bar{1}10$	65° 44	
	$\bar{1}10$ " $\bar{1}\bar{1}0$	48° 28′	48° 40′
	$\bar{1}10$ " $0\bar{1}0$	65° 52½′	
	$0\bar{1}0$ " $1\bar{1}0$	65° 35′	
	$1\bar{1}0$ " 110	48° 44′	
		359° 56½′	
Zone [010, 011]	010 and 011	63° 11′	63° 14′
	011 " 011	54° 5′	53° 33′
	$0\bar{1}1$ " $0\bar{1}0$	62° 56′	

It also gave the percentage of bromine required for tribromacrylic acid.

0.1553 gram substance gave 0.2819 gram AgBr.

	Calculated for $C_3HBr_3O_2$.	Found.
Br	77.66	77.25

Chlorbromiodacrylic Acid.

Chlorbromiodacrylic acid may be prepared most conveniently by heating brompropiolic acid with an ethereal solution of iodine monochloride, although without the application of heat the reaction takes place slowly. Iodine monochloride was made according to the method proposed by Bunsen.[2] The calculated weight of iodine was dissolved in aqua regia with the aid of heat, and after cooling the solution was extracted with ether and washed thoroughly with water. When brompropiolic acid is heated for an hour with this solution, the oily liquid left on evaporation of the ether soon deposits large prismatic crystals of the addition-product. For purification the crude product was pressed in filter-paper and recrystallized from hot water.

[1] Proceedings American Academy, **16**, 216.

[2] Annalen der Chemie, **74**, 8.

This substance is readily soluble in ether and alcohol, somewhat less so in carbonic disulphide and chloroform. From a hot aqueous solution it separates as an oil which crystallizes on cooling in rhombic prisms of the monoclinic system. By crystallization from water we did not succeed in raising the melting point above 110°; but the crystals formed by slow evaporation of a solution in carbonic disulphide melted at 115°–116°. It sublimes freely at somewhat higher temperatures.

This acid was identified by the following analyses:

I. 0.6743 gram substance gave 0.2843 gram CO_2.[1]

II. 0.1505 gram substance gave 0.2721 gram $AgCl+AgBr+AgI$.

	Calculated for $C_3HClBrIO_2$.	Found. I.	Found. II.
C	11.55	11.50	
H	.32		
$Cl+Br+I$	77.84		77.41

The following results were obtained in determining the solubility in cold water:

I. 8.1470 grams of a solution saturated at 20° gave 0.1396 gram $BaSO_4$.

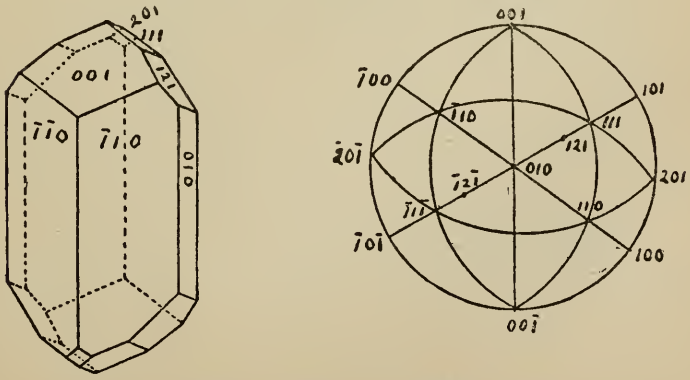
II. 5.4630 grams of a solution saturated at 20° gave 0.0968 gram $BaSO_4$.

From these results were calculated the percentages:

I.	II.
4.58	4.74

For a determination of the crystalline form of this acid we are indebted to the kindness of Dr. Melville, who obtained the following results:

CRYSTALLINE FORM OF CHLORBROMIODACRYLIC ACID.



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[1] By an accident the water in this combustion was lost.

MONOCLINIC SYSTEM.

Forms [001], [010], [110], [121], [111], [201].

Elements:—Clinodiagonal, $a = 0.594$
Orthodiagonal, $b = 1.$
Vertical Axis, $c = 0.572$
Angle of axes XZ = 52° 47′

				Observed.	Calculated.
Angles between normals	111	and	110	58° 23′	Fundamental angles.
	121	"	110	55° 45′	
	121	"	101	43° 48′	
	111	"	010	62° 43′	62° 28′
	110	"	001	123° 26′	123° 13′
	110	"	010	65° 3′	64° 56′
	111	"	110	82° 24′	82° 23′

It will be seen by inspection of the forms of dibromiodacrylic and chlorbromiodacrylic acids that these substances present a striking instance of isomorphism. In fact the only form not common to both is that of [201], which was not observed on the crystals of dibromiodacrylic acid. This similarity in form, which extends also to tribromacrylic acid, is rendered more prominent by a comparison of the observed angles. The measurements of tribromacrylic acid show a greater variation in the observed angles except in case of the angle which the prism [110] makes with the pinacoid [010].

			Dibromiodacrylic acid.	Chlorbromiodacrylic acid.	Tribromacrylic acid.
110	and	010	64° 3′	65° 3′	65° 33
110	"	110	128°	130° 6′	
110	"	001	123° 26′	123° 26′	
111	"	010	62° 11′	62° 43′	
111	"	110	59° 14½′	58° 23′	
121	"	010	42° 59′	43° 48′	
121	"	110	55° 59′	55° 45′	

The elements of the crystals also proved to be nearly identical.

	Dibromiodacrylic acid.	Chlorbromiodacrylic acid.
Clinodiagonal a	0.617	0.594
Orthodiagonal b	1.	1.
Vertical axis c	0.581	0.572
Angle of axes XZ	52° 11½′	52° 47′

A study was made of some of the more important salts of chlorbromiodacrylic acid.

Baric chlorbromiodacrylate $Ba(C_3ClBrIO_2)_2.3\frac{1}{2}H_2O$.

A solution of the acid was saturated with baric carbonate, filtered, and concentrated on the water-bath. The salt separated on cooling in rectangular prisms, which, when dried by exposure to the air, contained three and a half molecules of crystal water. It is quite soluble in cold, and very soluble in hot water.

I. 0.8250 gram of the air-dried salt lost when heated to 80° 0.0636 gram H_2O.

II. 0.7273 gram of the air-dried salt lost at 80° 0.0540 gram H_2O.

III. 0.5401 gram of the air-dried salt lost at 80° 0.0384 gram H_2O.

IV. 0.5502 gram of the air-dried salt lost at 80° 0.0438 gram H_2O.

V. 0.6697 gram of the anhydrous salt gave on ignition with H_2SO_4 0.2080 gram $BaSO_4$.

VI. 0.5032 gram of the anhydrous salt gave 0.1570 gram $BaSO_4$.

VII. 0.4959 gram of the anhydrous salt gave 0.1527 gram $BaSO_4$.

	Calculated for $Ba(C_3ClBrIO_2)_2.3\frac{1}{2}H_2O$.	Found.			
		I.	II.	III.	IV.
H_2O	7.67	7.71	7.44	7.11	7.96

	Calculated for $Ba(C_3ClBrIO_2)_2$.	Found.		
		V.	VI.	VII.
Ba	18.07	18.26	18.34	18.10

The solubility at 20° was determined by evaporating a saturated solution to dryness and igniting the residue with sulphuric acid.

I. 3.7500 grams solution gave 0.2339 gram $BaSO_4$.

II. 3.1458 grams solution gave 0.1957 gram $BaSO_4$.

According to these determinations a solution saturated at 20° contains the percentages:

I.	II.
20.30	20.23

Calcic chlorbromiodacrylate $Ca(C_3ClBrIO_2)_2.H_2O$.

When a solution of the acid is neutralized with calcic carbonate, and the filtered solution concentrated by evaporation, the calcium salt separates in the form of branching needles. The air-dried salt contains one molecule of crystal water, which it loses at 80°.

I. 0.7180 gram of the air-dried salt lost 0.02116 gram H_2O at 80°.

II. 0.6770 gram of the air-dried salt lost 0.0197 gram H_2O at 80°.

III. 0.6583 gram of the anhydrous salt gave 0.1404 gram $CaSO_4$.

	Calculated for $Ca(C_3ClBrIO_2)_2.H_2O$.	Found.	
		I.	II.
H_2O	2.66	3.01	2.91

	Calculated for $Ca(C_3ClBrIO_2)_2$.	Found.
		III.
Ca	6.05	2.91

Potassic chlorbromiodacrylate $KC_3ClBrIO_2$?

The potassium salt is obtained as a very deliquescent solid mass by evaporating a solution of the acid after neutralizing with potassic carbonate.

0.8076 gram of the salt dried at 80° gave on ignition with H_2SO_4 0.2176 gram K_2SO_4.

	Calculated for $KC_3ClBrIO_2$.	Found.
K	11.19	11.27

Argentic chlorbromiodacrylate $AgC_3ClBrIO_2$.

The silver salt was prepared by the addition of argentic nitrate to a hot aqueous solution of the acid. It crystallizes in rhombic prisms, which are quite soluble in hot, sparingly soluble in cold water.

I. 0.5383 gram of the salt gave 0.1825 gram AgCl.

II. 0.5129 gram of the salt gave 0.1766 gram AgCl.

	Calculated for $AgC_3ClBrIO_2$.	Found.	
		I.	II.
Ag	25.80	25.52	25.91

XIX.—PRELIMINARY NOTICE OF ORTHOIODBENZYLBROMIDE AND ITS DERIVATIVES.[1]

BY CHARLES F. MABERY AND FRANKLIN C. ROBINSON.

Orthoiodbenzylbromide is formed when bromine is allowed to act on orthoiodtoluol at temperatures near its boiling point. In the preparation of orthoiodtoluol we obtained the most satisfactory results from the sulphate of orthodiazotoluol. Orthotoluidin from the factory of Kahlbaum at Berlin was treated in quantities of 10 grams each, with two molecules of sulphuric acid, and to this mixture (cooled to 0°) was added gradually a solution of one molecule of sodic nitrite. On the addition of hydriodic acid (boiling point 127°) in slight excess over the calculated amount for the solution of the diazo-compound thus obtained, orthoiodtoluol was precipitated as a heavy oily liquid. The crude product was washed with sodic hydrate and acetic acid, and lastly with water. It was then dried over calcic chloride, and finally purified by fractional distillation. In this way from 20 grams orthotoluidin we obtained before fractioning 28 grams orthoiodtoluol, which gave 20 grams boiling at 211° (mercury column wholly in vapor).[2]

To convert orthoiodtoluol into orthoiodbenzylbromide, 10 grams were heated to 190°–200° under a return condenser, and 10 grams bromine allowed to run into the flask from a drop funnel as rapidly as it was absorbed. On cooling, the product of the reaction formed a thick oily liquid which did not solidify at 0°. It was therefore washed with a dilute solution of sodic hydrate, to remove the iodine which was invariably set free during the bromiring, and distilled in the vapor of concentrated hydrobromic acid according to the method followed by Professor Jackson in the purification of orthobrombenzylbromide.[3] The distillate solidified when cooled with snow, and after removing the oil by pressure in filter-paper, it purified by crystallization from ligroin.

The composition of this substance was established by the following analyses:

I. 0.1994 gram of the substance gave 0.3945 gram AgBr+AgI.

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[1] Since Professor Jackson decided not to include orthoiodbenzylbromide in his researches on the substituted benzyl compounds, we have undertaken its study.—(C. F. M.)

[2] Kekulé, Berichte der deutschen chemischen Gesellschaft, 7, 1007.

[3] Proceedings American Academy, 12, 217.

II. 0.2793 gram of the substance gave 0.3945 gram AgBr + AgI.

III. 0.3246 gram of the substance gave 0.3350 gram CO_2 and 0.0674 gram H_2O.

	Calculated for C_7H_6BrI.	Found.		
		I.	II.	III.
C	28.28			18.16
H	2.02			2.30
Br + I	69.68	69.53	69.11	

Orthoiodbenzylbromide is readily soluble in ether, hot alcohol, benzol, carbonic disulphide, and chloroform. It is nearly, if not quite, insoluble in water, and very sparingly soluble in cold ligroin. From a cold saturated solution in ligroin it crystallizes by slow evaporation in flattened prisms often 2 or 3 centimeters in length. When crystallization takes place from a hot solution it appears in the form of short thick prisms. The vapor of this substance affects the mucous membrane in the same way as that of all the benzyl compounds thus far examined, and it seems to be far more volatile than the corresponding para compound. It melts at 52°–53°, and at higher temperatures sublimes slowly in oily drops which soon solidify in radiating needles. By oxidation with dilute nitric acid it is converted into an acid which melts at 150°–155°. Since the orthoiodbenzoic acid obtained by Kekulé[1] from orthoiodtoluol melted at 155°–156°, our product without doubt has the same composition.

As a further proof of the constitution of orthoiodbenzylbromide we made the nitril, and from it orthoiodalphatoluic acid. To form the nitril the bromide was boiled with an alcoholic solution of potassic cyanide. The oily liquid precipitated by the addition of water was heated to 125° for four hours with fuming hydrochloric acid. When cold the oil solidified, and more of the acid separated from the solution in long needles. After removing the excess of hydrochloric acid, the crude product was purified by crystallization from hot water.

Orthoiodalphatoluic acid crystallizes in fine felted needles which are sparingly soluble in cold, readily soluble in hot water and in alcohol, ether, carbonic disulphide, and ligroin. With the limited amount of material at our disposal we were unable to raise the melting point above 95°–96°. It would seem, however, from the analogy of the orthobromalphatoluic acid that the melting point of our acid should be somewhat higher. When we return to this subject and have access to a larger supply of the acid, its melting point will be more carefully tested. The silver salt of this acid was made by adding argentic nitrate to an aqueous solution of the ammonium salt. It separated from the solution as a curdy precipitate which was but slightly soluble in water, readily soluble in dilute nitric acid. For analysis it was dried over sulphuric acid.

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[1] Berichte der deutschen chemischen Gesellschaft, 7, 1007.

0.2615 gram of the salt gave by precipitation with HCl 0.1008 gram AgCl.

	Calculated for $C_7H_6ICOOAg$.	Found.
Ag	29.27	29.00

We also submitted the bromide to the action of alcoholic ammonia; but as the result of one experiment with a small quantity of substance we succeeded in isolating only the primary amine. The product of this reaction was treated with water, and the aqueous solution evaporated on the water-bath. Upon the addition of sodic hydrate the free base was partially precipitated as an oily liquid, and more of the oil was obtained by extracting the solution with ether. The residue left by evaporation of the ether was immediately converted into the carbonate by absorbing carbonic dioxide from the air. It was dissolved in alcohol, a little hydrochloric acid added, and the platinum salt formed by the addition of chlorplatinic acid. This salt crystallized in pale yellow microscopic prisms, which were sparingly soluble in water and cold alcohol, readily in hot, and insoluble in ether. It was purified by recrystallization from hot alcohol, washed with ether, and dried over sulphuric acid for analysis.

0.2082 gram of the salt gave on ignition 0.0468 gram platinum.

	Calculated for $(C_7H_6INH_3)_2PtCl_6$.	Found.
Pt	22.48	22.48

Since our work was interrupted by the closing of the summer term a more complete examination of the derivatives of orthoiodbenzylbromide must be reserved for another paper.

XX.—CHLORTRIBROMPROPIONIC ACID.

By Charles F. Mabery and H. C. Weber.

The formation of chlortribrompropionic acid by the action of bromine on chlorbromacrylic acid has been mentioned in a previous paper by R. Lloyd and one of us.[1] Although this reaction took place without difficulty in a chloroform solution at ordinary temperatures, the product proved to consist in great part of an oil which could not be made to crystallize. With the hope of obtaining a more satisfactory yield we tried the action of undiluted bromine at a higher temperature. Chlorbromacrylic acid, melting point 68°–70°, with a slight excess over the calculated weight of bromine, was heated to 100° for two hours in a closed tube. The excess of bromine was removed by spontaneous evaporation from the product, which was purified by pressure between folds of filter paper and crystallization from carbonic disulphide. By this method from 6.5 grams chlorbromacrylic acid we obtained 8.5 grams essentially pure chlortribrompropionic acid, or about seventy per cent. of the theoretical amount.

This acid is readily soluble in ether and alcohol, less soluble in cold than in hot carbonic disulphide and chloroform. In contact with water it forms an oil which does not solidify at 0°. From carbonic disulphide or chloroform it crystallizes by slow evaporation in oblique prisms of the triclinic system which melt at 102°–103°. In the analysis of this substance the following results were obtained:

I. 0.1582 gram of the substance gave by the method of Carius, 0.3234 gram $AgCl+AgBr$.

II. 0.1582 gram of the substance gave 0.3251 gram $AgCl+AgBr$.

III. 0.9373 gram of the substance gave 1.9049 gram $AgCl+AgBr$. 1.9003 gram $AgCl+AgBr$ gave 1.1568 gram Ag.[2]

IV. 0.8096 gram of the substance gave 0.3065 gram CO_2 and 0.0631 gram H_2O.

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[1] This Journal, **3**, 124; and Proceedings American Academy, **16**, 240.

[2] This determination was made with the aid of the excellent method devised by Mr. L. P. Kinnicutt. (This Journal, **4**, 22; and Proceedings American Academy, **16**, 91.)

	Calculated for $C_3H_2ClBr_3O_2$.		Found. I.	II.	III.		IV.
C	10.42						10.32
H	.58						.87
Cl+3Br	79.75		79.58	80.00			
Cl	10.28	79.75			9.62	79.36	
Br	69.47				69.74		

The barium, calcium and potassium salts of this acid were made and analyzed.

Baric chlortribrompropionate $Ba(C_3HClBr_3O_2)_2$.

To form the barium salt a solution of the acid was neutralized with baric carbonate and baric hydrate, filtered, and concentrated by spontaneous evaporation at the ordinary temperature. The salt crystallized in slender oblique prisms, which were quite soluble in cold water. The air-dried salt was constant when heated to 80°.

I. 0.6933 gram of the salt dried at 80° gave on ignition with H_2SO_4 0.1920 gram $BaSO_4$.

II. 0.6440 gram of the salt dried at 80° gave 0.1793 gram $BaSO_4$.

	Calculated for $Ba(C_3HClBr_3O_2)_2$.	Found. I.	II.
Ba	16.59	16.26	16.37

The solubility of this salt we determined by the method of V. Meyer. A saturated solution was kept at 20° for three hours, filtered, evaporated to dryness, and the residue ignited with sulphuric acid.

I. 1.8400 gram solution gave 0.0977 gram $BaSO_4$.

II. 0.8926 gram solution gave 0.0470 gram $BaSO_4$.

These results correspond to the percentages:

I.	II.
18.82	18.66

Calcic chlortribrompropionate $Ca(C_3HClBr_3O_2)_2$.

To prepare the calcium salt we neutralized a solution of the acid with calcic carbonate and calcic hydrate, and allowed the filtered solution to evaporate spontaneously. From the concentrated solution the salt separated in clustered needles, which, when air-dried, were constant at 80°.

1.0691 gram of the salt dried at 80° gave on ignition with H_2SO_4 0.1883 gram $CaSO_4$.

	Calculated for $Ca(C_3HClBr_3O_2)_2$.	Found.
Ca	5.49	5.25

Potassic chlortribrompropionate $KC_3HClBr_3O_2.H_2O$.

The potassium salt was made by neutralizing a solution of the acid with potassic carbonate and evaporating at the ordinary temperature. This salt crystallized in rhombic prisms which are freely soluble in cold water. It contained one molecule of crystal water which was given up over sulphuric acid.

I. 1.0688 gram air-dried salt gave 0.0502 gram H_2O.
II. 1.0428 gram air-dried salt gave 0.0490 gram H_2O.
III. 0.9802 gram of the anhydrous salt gave 0.2201 gram K_2SO_4.

Calculated for $KC_3HClBr_3O_2.H_2O$.		Found. I.	Found. II.
H_2O	4.48	4.70	4.72

Calculated for $KC_3HClBr_3O_2$.		Found. III.
K	10.20	10.08

The silver salt of this acid proved to be so unstable that we did not succeed in preparing it in a form sufficiently pure for analysis. On the addition of argentic nitrate to an aqueous solution of the acid, even in the cold it immediately became turbid from the separation of argentic chloride.

Although the barium salt is comparatively stable, we found that it was slowly decomposed when heated in aqueous solution. In order to identify the products of this decomposition, the acid was distilled with an excess of baric hydrate. The distillate was caught in bromine water, the excess of bromine allowed to evaporate, and the solution extracted with ether. The oily residue left by evaporation of the ether solidified at 0°, and possessed an odor characteristic of the substituted ethans. It would seem probable, therefore, that the volatile product of this decomposition was tribromethylen; but it was formed in such small quantity that further study was rendered extremely difficult. The residue in the retort contained baric chloride in abundance, but it gave no reaction for baric bromide. The formation of tribromacrylic acid is thus rendered extremely probable; but the residue unfortunately was lost before it could be subjected to a more critical examination. Since the summer term soon after closed, we were unable to repeat our work, and it must therefore be reserved for future study.

Chlorbromacrylic acid forms also an addition-product with hydrobromic acid. When it is heated to 100° in a closed tube with concentrated hydrobromic acid, an acid is formed which melts at 80°. Further study of this substance, which is probably chlordibrompropionic acid, will be postponed for the present.

Contributions from the Sheffield Laboratory of Yale College.

XII.—INFLUENCE OF PEPTONES AND CERTAIN INORGANIC SALTS ON THE DIASTATIC ACTION OF SALIVA.

By R. H. Chittenden and J. S. Ely.

Recent experiments[1] on the diastatic action of saliva under various conditions have revealed the fact that human mixed saliva in the presence of an equal volume of artificial gastric juice containing .05 per cent. of hydrochloric acid, is capable of forming, from a given quantity of starch, a much larger amount of sugar than the same quantity of saliva alone can do under a like degree of dilution; this being the more remarkable when it is remembered that the same percentage of acid by itself greatly retards the diastatic action. This somewhat curious fact has led us to study the individual influence of several bodies of physiological importance on salivary fermentation. It is our conviction that many of the digestive processes of the body are more dependent for their fullest action on the stimulating or other influence caused by the mere presence of many of the digestive products, than has hitherto been supposed. Experiment, to be sure, has revealed the fact that several of the products of digestion when present in the digestive mixture in excess, notably sugar in the case of salivary digestion and peptones in gastric digestion, retard the digestive process. Under ordinary circumstances, however, all conditions are favorable, in the normal body, for a rapid absorption of the digestive products, and thus any excessive accumulation is prevented. Schmidt-Mülheim[2] found in his recent study of proteid digestion, that in the case of dogs, the quantity of peptones present in the stomach was practically the same at all times during the digestion; thus 1, 4 and 6 hours after feeding a dog 61 grams of albumin, the stomach contained 3.08 grams, 3.31 grams and 2.91 grams of peptones respectively, which would seem to indicate that after the formation of a definite quantity of the digestive products the transportation of these bodies keeps pace with the digestion. Again, there are no facts to warrant the belief that the products of one digestive process necessarily hinder the action of some other allied ferment; indeed, it is ordinarily understood that any accumulation of the digestive products simply hinders the action of that particular ferment by clogging the digestive fluid.

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[1] Chittenden and Griswold, this Journal, 3, 305.

[2] Untersuchungen über die Verdauung der Eiweisskörper, Du Bois Reymond's Archiv f. Physiologie, 1879, 39.

There is nothing inconsistent then in the statement that the products of one digestion may act as a stimulant to some other digestive process. The results of the experiments about to be described show plainly that *peptones, a product of gastric digestion, exercise a decided influence on salivary digestion, stimulating the ferment to increased action, particularly in the presence of acid which by itself completely prevents the conversion of starch into sugar.* If now we are led, in virtue of this fact, to infer that there may be a possible continuation of salivary digestion in the stomach, it follows that the ferment must act at the first period of digestion, when the acid fluids are exceedingly weak. The fact that the quantity of peptones present in the stomach at this stage of digestion may be quite small offers no objection whatever to a possible action of the peptones, since the experiments already quoted, and those about to be described, well illustrate how extremely sensitive the saliva is to a change of conditions however slight; thus even minute quantities of inorganic salts, even to the extent of only .015 per cent., exercise a decided influence on ferment action.

We may also reasonably infer that the saliva is, to a certain extent, a type of the other diastatic fluids of the body, and that the ferment itself is doubtless similar in its action to other like ferments, notably the ferment or ferments of the liver, which presumably convert the glycogen of the hepatic cells into sugar. Thus conditions which modify the diastatic action of saliva may not be wholly without similar influence on other like ferments. It has, therefore, seemed to us that the results of our work may have some bearing upon the recently published experiments of Seegen,[1] of Vienna, who found that when an aqueous solution of peptones was poured over a small piece of fresh liver, the quantity of sugar formed in a specified time was greater than in a piece of the same liver treated in a like manner but without peptones; at the same time however, the total amount of carbohydrate matter appeared to be increased in the presence of the peptones. Finding that the peptones themselves had no diastatic action on glycogen, Seegen then concluded that the liver possesses the power of transforming peptones into sugar and carbohydrates which are capable of being converted into sugar. While our results may in nowise affect Seegen's conclusions, they certainly suggest the possibility that the increase of sugar noticed in the presence of the peptones may be due, in part at least, to some cause other than that attributed by Seegen.

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[1] Die Einwirkung der Leber auf Pepton, Pflüger's Archiv, 25, 165.

We have attempted at first in our experiments to ascertain whether by themselves or under such conditions as may presumably exist in the body, peptones have any influence on the conversion of amylaceous matter into sugar by the saliva. The amylaceous material employed was starch and glycogen, while the diastatic agent was human mixed saliva, which was usually collected in quantities of 150–250 cc. by the chewing of some tasteless substance, then filtered and thoroughly mixed before using. The saliva was ordinarily used an hour or two after collecting, and being as a rule always furnished by the same person, possessed approximately the same strength, although control experiments with starch and saliva alone under a like degree of dilution were made in each case. The method employed consisted in dissolving a weighed amount of starch or glycogen in 25 cc. of water, then adding 50 cc. of water or other fluid in which a weighed quantity of peptone or other substance was dissolved, and lastly 25 cc. of filtered saliva. The mixture, consisting of 100 cc. of fluid, was then warmed for a definite time, usually 45 minutes, at 40° C., when further action was prevented by boiling the mixture. The fluid was then diluted with water to 500 cc., and when thoroughly mixed, 50 cc. or one-tenth of the filtered fluid was precipitated by cupro-potassium tartrate, according to the method of Maercker, described in another place.[1] The copper was weighed as metallic copper, from which the percentage of reducing substance calculated as dextrose was determined by the use of Maercker's tables.

Influence of Peptones in Aqueous Solution.

The peptones employed were prepared especially for the purpose and were made as pure as possible. Three samples were prepared from thoroughly washed blood-fibrin by the action of an active gastric juice made from a glycerin extract of pepsin and .2 per cent. hydrochloric acid, while the fourth was made from coagulated egg-albumin by the use of a similar gastric juice. All four preparations were the products of an active digestion, and were therefore free from syntonin or other preliminary products. The peptones were purified by repeated precipitation and standing under alcohol and ether, while the fourth was especially purified from soluble salts by dialysis. The following results show plainly the action of the peptones. In each experiment 1 gram of the dried peptones dissolved in 50 cc. of water was added to 1 gram of starch previously boiled with 25 cc. of water, the 25 cc. of saliva making a digestive mixture of 100 cc., in which the peptones were present to the extent of 1 per cent. In the control experiment the mixture was made up to the same volume with water. Different saliva was used in each experiment.

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[1] This Journal, **3**, 307.

	Without Peptones.		*With Peptones.*	
Number of experiment.	Wt. Cu in one-tenth.	Total amount of sugar.	Wt. Cu in one-tenth.	Total amount of sugar.
1.	.0896 gram	.4557 gram	.0962 gram	.4893 gram
2.	.0911 "	.4633 "	.0974 "	.4954 "
3.	.0915 "	.4654 "	.1045 "	.5315 "
4.	.0904 "	.4598 "	.0977 "	.4969 "
5.	.0856 "	.4354 "	.0937 "	.4766 "
6.	.0835 "	.4247 "	.0949 "	.4826 "

The increased diastatic action of the saliva in the presence of the peptones is made more plainly apparent by the following table, in which are given the percentage amounts of starch converted into sugar; calling the sugar $C_6H_{12}O_6$ and the starch $C_6H_{10}O_5$.

	Without Peptones.	*With Peptones.*
1.	41.01 per cent.	44.03 per cent.
2.	41.69 "	44.58 "
3.	41.88 "	47.83 "
4.	41.38 "	44.72 "
5.	39.13 "	42.89 "
6.	38.22 "	43.43 "

It is thus seen that the presence of 1 per cent. of peptones causes an increased conversion of starch into sugar, amounting on an average to 4 per cent.

Similar experiments made with glycogen yielded like results. 2 grams of pure, dried glycogen prepared from *Pecten irradians*[1] were employed in each experiment, and the digestions continued for 30 minutes. 1 gram of peptones was used as before.

	Without Peptones.		*With Peptones.*	
	Wt. Cu in one-tenth.	Total amount of sugar.	Wt. Cu in one-tenth.	Total amount. of sugar.
1.	.1405 gram	.7297 gram	.1477 gram	.7671 gram
2.	.1286 "	.6581 "	.1386 "	.7144 "
3.	.1300 "	.6653 "	.1328 "	.6771 "
4.	.1281 "	.6556 "	.1306 "	.6684 "

A few experiments were then tried, both with glycogen and starch, using 2 grams of peptones. Following are the results:

	Without Peptones.	*With 1 gram Peptones.*	*With 2 grams Peptones.*
	Wt. Cu in one-tenth.	Wt. Cu in one-tenth.	Wt. Cu in one-tenth.
Starch	.0835 gram	.0949 gram	.0960 gram
Glycogen	.1405 "	.1477 "	.1472 "
"	.1286 "	.1386 "	.1429 "
"	.1300 "	.1328 "	.1362 "

Here it is to be noticed that the presence of 2 per cent. of peptones has but little additional influence on the diastatic action. That peptones themselves were entirely free from carbohydrate matter and that the saliva is wholly without action on the peptones was clearly shown by digesting 2 grams of peptones with 25 cc. of saliva. This experiment was repeated twice, but in neither case was any reduction obtained on boiling the diluted fluid with Fehling's solution. Again, the possibility suggested itself that the peptones might exercise some influence on the precipitation of the copper, and that the increase of copper obtained when peptones were present was due not to any stimulating action they might exert on the ferment, but to a precipitation or reduction of the copper. In order to settle this point three digestions were made in the usual manner with 2 grams of glycogen. No. 1 contained, in addition, 2 grams of peptones. No. 2 had added to it after the destruction of the ferment by boiling, 2 grams of peptones, while No. 3 served as a control. A determination of the amount of sugar in the aliquoted fluids gave the following results, clearly showing that the mere presence of the peptones has no influence on the precipitation of the copper :

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[1] Chittenden, Amer. Jour. Science and Arts, **10**, 26.

No. 1. Wt. Cu in one-tenth.	No. 2. Wt. Cu in one-tenth.	No. 3. Wt. Cu in one-tenth.
.1472 gram	.1403 gram	.1405 gram

There still remained two possible chances of error, viz. the possibility of the peptones containing a trace of a diastatic ferment or of their possessing a diastatic action, and secondly that the slightly acid reaction of the peptone solutions might exert some modifying influence. The former supposition was easily disproved by making a digestion of starch and peptones alone. This led, as would naturally be expected, to a negative result ; the solution showing no reducing action whatever. An endeavor was then made to obtain the same result in a somewhat different manner : a series of digestions was made, in which one of the peptone solutions was vigorously boiled before being added to the starch solution, the digestions then being made in the usual manner.

	Without Peptones. Wt. Cu in one-tenth.	*With 1 gram Peptones.* Wt. Cu in one-tenth.	*Peptone sol. boiled.* Wt. Cu in one-tenth.	*Peptone sol. boiled and water replaced.* Wt. Cu in one-tenth.
No. 1.	.0856 gram	.0937 gram	.0950 gram	.0952 gram
No. 2.	.0904 "	.0977 "	.1035 "	...

That the peptones contain no ferment is plainly apparent, but the slight increase of sugar when the peptone solution is boiled is certainly somewhat singular. Three of the peptones employed in these experiments gave, when dissolved in water, very faintly acid solutions. The acidity of 1 gram of peptones, however, was never sufficient to neutralize the alkali of 25 cc. of saliva.[1] The fourth sample, which was purified by dialysis, gave a neutral solution, and this sample did not differ in its action in the least from the other three. An attempt was made, however, to neutralize one of the peptone solutions, previous to the digestion, by the use of an exceedingly dilute alkali. The following results were obtained :

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[1] Neutral saliva appears to have as great a diastatic action as saliva of normal alkalinity. Thus while a digestion made with freshly collected alkaline saliva gave .0905 gram Cu, a portion of the same saliva neutralized gave .0943 gram Cu under the same conditions.

Without Peptones.	*With* 1 *gram Peptones.*	*With* 1 *gram neutralized Peptones.*
Wt. Cu in one-tenth.	Wt. Cu in one-tenth.	Wt. Cu in one-tenth.
.0915 gram	.1045 gram	.0991 gram

The slight decrease of copper in the neutralized peptone, as later experiments would seem to indicate, is due probably to the retarding influence of the alkali salt formed by neutralization, although it seems hardly possible that such a minute trace could exert any influence whatever on the action of the saliva.

O. Nasse[1] in his work on unformed ferments, found that in 4 per cent. solutions of certain inorganic salts there was an increased ferment action. It therefore seemed desirable to ascertain in the present case whether the inorganic salts contained in the peptones could exert any influence on the salivary ferment. The four samples of peptones contained the following percentages of ash:

No. 1.	No. 2.	No. 3.	No. 4.
1.71 per cent.	0.89 per cent.	1.25 per cent.	1.58 per cent.

With the exception of No. 4, the ash was composed of sodium chloride, sodium phosphate and calcium phosphate.

No. 4, which was prepared from coagulated albumin and purified by dialysis, left an ash composed wholly of calcium phosphate. The following results show the individual influence of the three inorganic salts on the diastatic action of saliva when present in the digestive fluid in approximately such percentages as the peptones give when added to the starch and saliva mixture:

FIRST EXPERIMENT.

	Wt. Cu in one-tenth.
Saliva and starch alone,	.0872 gram
" " +.012 gram NaCl = .012 per cent.	.0862 "
" " +.024 " " = .024 "	.0925 "
" " +.012 " Na_2HPO_4 = .012 per ct.	.0886 "
" " +.024 " " = .024 "	.0834 "

SECOND EXPERIMENT.

	Wt. Cu in one-tenth.
Saliva and starch alone,	.0844 gram
" " +.015 gram $CaHPO_4$ = .015 per cent.	.0839 "
" " +.030 " " = .030 "	.0870 "

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[1] Untersuchungen über die ungeformten Fermenten, Pflüger's Archiv, **11**, 138.

From these results it is apparent that no one of the inorganic salts of the peptones is present in sufficient quantity to have any stimulating action whatever in aqueous solution, for increased diastatic action is noticed only in the presence of 24 milligrams of sodium chloride, an amount much larger than the total ash of 1 gram of peptones. Again, peptone No. 4, which was freed from all trace of chloride by dialysis, had exactly the same stimulating effect as the other samples.

In order to ascertain exactly what the influence of the *mixture* of inorganic salts, as present in the peptones, would be, a series of digestions was made, in two of which the ash of 1 gram and of 2 grams of peptones respectively were employed; the ash, as in the experiments with the peptones themselves, being dissolved in 50 cc. of water, and in this manner added to the starch solution previous to the addition of the 25 cc. of saliva. The peptones employed were the ones which contained 1.71 per cent. of ash; thus the digestive mixtures contained respectively .017 and .034 per cent. of inorganic matter. The following results were obtained:

Saliva and Starch alone.	*With Ash from* 1 *gram Peptones.*	*With Ash from* 2 *grams of Peptones.*
Wt. Cu in one-tenth.	Wt. Cu in one-tenth.	Wt. Cu in one-tenth.
.0862 gram	.0851 gram	.0715 gram

It is thus very apparent that the stimulating action of the peptones is not due to the inorganic salts contained in them, for these latter, as the foregoing experiment shows, have, by themselves, in aqueous solution, a retarding influence. We therefore deem it proven that peptones under such conditions as have already been described have in aqueous solution a stimulating influence on salivary digestion. In other words, peptones when present to the extent of 1–2 per cent. cause, under the same conditions as saliva alone, an increased conversion of starch into sugar amounting on an average to 4 per cent.

Influence of Peptones in Acid Solution.

Previous experiments[1] have plainly demonstrated the extreme sensitiveness of the saliva to the action of dilute acids. Thus the addition of 50 cc. of .05 per cent. hydrochloric acid to a digestive mixture, thereby making the fluid contain but .025 per cent. of acid, very greatly diminishes the diastatic action. This result has been recently verified by J. N. Langley,[1] as also the results of Chittenden and Griswold in regard to the destruction of the salivary ferment by gastric juice and by .2 per cent. hydrochloric acid at 40°C.

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[1] Chittenden and Griswold, this Journal, **3**, 313.

An attempt was now made to ascertain the influence of peptones in an acid solution of the above strength, viz. .025 per cent. The experiments were conducted in the same manner as the preceding, with this exception: the peptones, instead of being dissolved in water, were in each case dissolved in 50 cc. of .05 per cent. hydrochloric acid. 1 gram of peptones was used in each experiment, starch being the amylaceous material employed.

	Saliva alone.		*Saliva and Acid.*		*Saliva, Acid and Peptones.*	
	Wt. Cu in one-tenth.	Total amount of sugar.	Wt. Cu in one-tenth.	Total amount of sugar.	Wt. Cu in one-tenth.	Total amount of sugar.
1.	.0896 gram	.4557 gram	.0076 gram	.0389 gram	.1068 gram	.5428 gram
2.	.0911 "	.4633 "	.0079 "	.0405 "	.1070 "	.5439 "
3.	.0915 "	.4654 "	.0098 "	.0502 "	.1060 "	.5388 "
4.	.0835 "	.4247 "	...	...	.0985 "	.5010 "

The percentage amounts of starch converted into sugar under the three conditions are as follows:

	Saliva alone.	*Saliva and Acid.*	*Saliva, Acid and Peptones.*
1.	41.01 per cent.	3.50 per cent.	48.85 per cent.
2.	41.69 "	3.64 "	48.95 "
3.	41.88 "	4.51 "	48.48 "
4.	38.22 "	...	45.09 "

Similar experiments were tried with glycogen, 2 grams of this substance being dissolved in 25 cc. of water and employed in the same manner as the starch; 1 gram of peptones was used as before. The following results were obtained:

	Saliva alone.	*Saliva and Acid.*	*Saliva, Acid and Peptones.*
	Wt. Cu in one-tenth.	Wt. Cu in one-tenth.	Wt. Cu in one-tenth.
1.	.1300 gram	.0049 gram	.1408 gram
2.	.1281 "	trace	.1424 "

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[1] Foster's Journal of Physiology, 3, 246.

It is thus seen that the presence of 1 gram of peptones exercises a very remarkable influence on the diastatic action of saliva in an acid solution of the above strength. The peptones are present in the digestive mixture to the extent of only 1 per cent., while the acid is but .025 per cent., yet this quantity of peptones is sufficient not only to counteract the retarding influence of the acid, but increases the conversion of the starch to the extent of 7 per cent. above the action of the saliva alone. Increasing the amount of peptones to 2 per cent. does not appear to have any effect whatever, as the following results show :

	1 *gram Peptones and* .025 *per cent. Acid.* Wt. Cu in one-tenth.	2 *grams Peptones and* .025 *per cent. Acid.* Wt. Cu in one-tenth.
1.	.1060 gram	.1084 gram
2.	.0985 "	.0974 "

In acid solutions of increased strength the peptones appear to exercise but slight if any influence; thus when the solution contained .1 per cent. hydrochloric acid, no diastatic action at all was observed, even in the presence of the peptones. In .05 per cent. acid solution however, one-tenth of the diluted and mixed digestive fluid yielded .013 gram Cu, showing a slightly increased action over and above what the acid fluid alone would give.

Control experiments with saliva, peptones and acid without starch yielded negative results, thus showing that the saliva is entirely without action on the peptones in an acid solution of the above strength. Again, digestions of starch, peptones and acid without saliva also gave negative results, proving that the peptones are wholly without diastatic action in the acid fluid. We deemed it advisable next to examine how far inorganic salts could influence the action of the ferment in an acid solution of the strength used. In aqueous solution it will be remembered the inorganic salts experimented with had but little or no action. In the acid solution the salts used were the same as before, viz. those present in the ash of the peptones. The experiments were conducted in the same manner as the preceding ; 100 cc. being the volume of the mixed fluid, of which 25 cc. were filtered saliva, 25 cc. water containing 1 gram of starch and 50 cc. .05 per cent. hydrochloric acid containing the salt.

FIRST EXPERIMENT.

	Wt. Cu in one-tenth.
Saliva and starch alone,	.0872 gram
" " +.05 per cent. HCl=.025 per cent.	.0088 "
" " " " " +.012 gram NaCl	.0132 "
" " " " " +.012 gram Na_2HPO_4	.0120 "

SECOND EXPERIMENT.

	Wt. Cu in one-tenth.
Saliva and starch alone,	.0835 gram
" " +.05 per cent. HCl = .025 per cent.	.0050 "
Saliva and starch+.05 per cent. HCl+.012 gram $CaHPO_4$	.0079 "
Saliva and starch+.05 per cent. HCl+.015 gram $CaHPO_4$	.0490 "
Saliva and starch+.05 per cent. HCl+.024 gram $CaHPO_4$	.0600 "

It is thus evident that sodium chloride and phosphate when present to the extent of .012 per cent. exercise but a very slight influence on the action of the saliva. Calcium phosphate, however, is seen to decidedly increase the diastatic action, though the amount contained in the peptones can have but little influence on the formation of sugar. Very striking is the great increase of sugar formed in the presence of 24 milligrams of calcium phosphate. This result is certainly suggestive of a possible utility of the calcium phosphate invariably present in wheat, oats and carbohydrate matter in general. What the exact explanation of the action of the phosphate in such a weak acid solution is, is of course hypothetical. The salt dissolves, in part at least, in the acid, and is thus probably modified with formation of bodies more favorable to the action of the ferment; it certainly cannot diminish to any extent the strength of the acid.

The influence of the combined inorganic matter of the peptones was now determined by experiment with the ash of No. 1, which contained 1.71 per cent.

	Saliva and Starch.	+.05 *per cent. HCl.*	+1 *gram Peptone.*	+*Ash* 1 *gram Peptone.*
	Wt. Cu in one-tenth.	Wt. Cu in one-tenth.	Wt. Cu in one-tenth.	Wt. Cu in one-tenth.
1.	.0866 gram	.0053 gram	.1058 gram	.0370 gram
2.	.0862 "	...	...	.0123 "

Thus, in the sample containing the largest percentage of ash, and presumably therefore of calcium phosphate, and under the same conditions as this salt appears to work to the best advantage, only a slight increase is noticed in the diastatic action of the saliva. It is therefore evident that while the addition of 50 cc. .05 per cent. hydrochloric acid to an equal volume of saliva and water brings the diastatic action down almost to zero, the addition of 1 gram of peptones to this acid fluid increases the diastatic action of the saliva to above its normal amount. In other words, the presence of 1 per cent. of gastric peptones in a salivary mixture containing .025 per cent. of acid acts as a stimulant to the diastatic ferment, causing it to act with greatly increased vigor. This fact appears to us to be of prime importance in solving the question as to the possibility of a continued action of the salivary ferment in the stomach. In 1881 one[1] of us, experimenting with human saliva, found that its diastatic action was increased by the presence of very minute quantities of hydrochloric acid: thus, while the quantity of sugar formed by freshly collected saliva was regarded as 100, the quantity formed by saliva of the same collecting in a mixture containing .005 per cent. of hydrochloric acid was 110. Increasing the percentage of acid diminishes the diastatic action, until at last, when the fluid contains .025 per cent. of hydrochloric acid, the formation of sugar is almost entirely stopped. Again, it was found[2] on digesting 25 cc. of human saliva with 50 cc. of gastric juice containing .2 per cent. of hydrochloric acid, at 40°C. for two hours, that the diastatic ferment was entirely destroyed; likewise that simple warming of the saliva with .2 per cent. acid at 40°C. for two hours was sufficient to destroy the greater part of the ferment, as was evinced by the low diastatic power of the neutralized fluid. Both of these results have received recent confirmation from the experiments of J. N. Langley[3] on the diastatic ferment of the parotid of rabbits. From his experiments he concludes that the ptyalin is destroyed by .2–.04 per cent. hydrochloric acid in from 7 to 24 hours at 40°C., and that the presence of .014 per cent. of acid is sufficient to destroy all but the merest trace of ferment in five minutes at 39°C. It appears to us, however, that in the case of human saliva at least there may be in the presence of a very dilute acid a simple stopping of the diastatic action without destruction of the ferment; thus, in the presence of

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[1] Chittenden and Griswold, this Journal, **3**, 305.

[2] Chittenden and Griswold, *loc. cit.*

[3] Foster's Journal of Physiology, **3**. 246.

.025 per cent. of acid there is but little diastatic action, but if that percentage of acid is sufficient to destroy the ferment in such a short time, in what manner does the 1 per cent. of peptones in an acid solution of the same strength cause such an increased formation of sugar? Again, the experiments of Chittenden and Griswold showed that by warming a mixture of starch, saliva and artificial gastric juice of weak acidity, at 40°C. for 45 minutes, the diastatic action of the saliva was greatly increased; thus, in the digestion of 1 gram of starch + 25 cc. of water + 50 cc. of gastric juice, containing .05 per cent. hydrochloric acid + 25 cc. saliva, the amount of sugar formed as compared with the amount found by the saliva alone was 133 : 100; while, as the present experiments show, the presence of .025 per cent. hydrochloric acid alone stops the action almost completely. It therefore seems probable that in the presence of such dilute acids as the above the ferment is simply hindered in its action, the presence of the peptones being sufficient to counteract the retarding influence of the acid. That this view as to the non-destruction of the ferment is correct, as regards human saliva at least, we think is plainly demonstrated by the following experiment. 75 cc. of filtered saliva were divided into three equal parts, which were treated as follows:

1st. 25 cc. saliva + 25 cc. .05 per cent. HCl warmed at 40°C. for 45 minutes. Solution then neutralized with Na_2CO_3. 1 gram of starch made into a paste with 50 cc. H_2O was then added and the mixture warmed at 40°C. for 45 minutes. Solution boiled and diluted to 500 cc. 50 cc. of this solution reduced .0862 gram Cu.

2d. 25 cc. saliva + 25 cc. H_2O + 50 cc. .05 per cent. HCl warmed at 40°C. for 45 minutes. Solution then neutralized with Na_2CO_3. 1 gram starch made into a paste with 25 cc. H_2O was then added and the mixture warmed at 40°C. for 45 minutes. Solution boiled and diluted to 500 cc. 50 cc. of this solution reduced .0805 gram Cu.

3d. 25 cc. saliva + 75 cc. H_2O warmed at 40°C. for 45 minutes. 1 gram of starch made into a paste with 25 cc. H_2O was then added and the mixture warmed at 40°C. for 45 minutes. Solution boiled and diluted to 500 cc. 50 cc. of this solution reduced .0824 gram Cu.

Here it is plainly seen that the ferment has not been in the least affected by the action of .025 per cent.[1] hydrochloric acid at this temperature. In the case of .1 or .2 per cent. acid the peptones are wholly without influence, since these strengths of acid are capable of destroying the ferment. It is evident that the salivary ferment is ultimately destroyed in the stomach by the gastric juice, but this fact does not necessarily preclude the possibility of a continued action of the saliva in the stomach. There is a growing impression that in the first stage of stomach digestion there is but little or no free acid present; thus Reinhard v. d. Velden[1] claims, as a result of observation, that for the first three-fourths of an hour after eating a hearty meal, human gastric juice fails to contain much if any free acid. It now seemed desirable to ascertain the rapidity with with starch is converted into sugar by the saliva. 125 cc. of filtered saliva were thoroughly mixed, and 12 cc. of this fluid were used in each experiment. The starchy solution was made by boiling .5 gram starch with 40 cc. of water, and to this solution the 12 cc. of saliva were added, making approximately 52 cc. of fluid. The mixtures were kept at a temperature of 40°C. for the specified time, then boiled to destroy the ferment. Each fluid was then diluted to 200 cc. and the sugar determined as before in 50 cc. of the mixed and filtered solution. Following are the results:

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[1] It should be mentioned here that the real percentage of acid is somewhat less than .025, owing to the slight alkalinity of the saliva. Ordinarily, however, the alkalinity is not so great in a sample of several hundred cubic centimeters as in a small quantity of freshly-secreted saliva. That there might be no possible chance of error, 25 cc. of mixed saliva were carefully neutral-

Period of digestion.	Wt. Cu in one-fourth.	Total amount sugar.	Percentage of starch converted into sugar.
1 minute	.0870 gram	.4425 gram	39.82 per cent.
5 minutes	.0963 "	.4898 "	44.09 "
10 "	.0991 "	.5040 "	45.36 "
15 "	.1005 "	.5111 "	45.99 "
30 "	.1040 "	.5286 "	47.57 "
45 "	.1087 "	.5525 "	49.72 "
1 hour	.1109 "	.5637 "	50.73 "
2 hours	.1147 "	.5842 "	52.57 "

This experiment makes it very apparent that by far the greater part of the starch is almost immediately converted into sugar. It seems therefore quite possible, especially in view of the action of peptones in a weak acid solution, that in the case of human beings

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ized with diluted hydrochloric acid. Then 25 cc. of .05 per cent. HCl were added, making an exactly .025 per cent. HCl solution. This mixture was then warmed at 40°C. for 45 minutes, after which it was exactly neutralized with Na_2CO_3 solution. One gram of starch in 50 cc. H_2O was then added and the whole warmed at 40°C. for 45 minutes; 50 cc. or one-tenth of the diluted fluid yielded .0882 gram Cu. Thus here, as in the above experiments, it is plainly evident, from the diastatic action of the neutralized saliva, that the ptyalin is not destroyed nor even affected by .025 per cent. of actual HCl under the above conditions.

[1] Zeitschrift f. physiolog. Chem. 3, 205.

there may be a continuation of salivary digestion in the stomach, provided the contents of the stomach during the first stage of digestion do not contain more than .025 per cent. of free acid.

Influence of Peptones in Alkaline Solution.

Previous experiments have demonstrated that the addition of sodium carbonate to saliva has a retarding influence on salivary digestion. It now seemed advisable to study the influence of peptones in the presence of dilute solutions of sodium carbonate, with especial reference to the pancreatic ptyalin, for presumably in the intestinal canal the diastatic ferment there present acts on starch in an alkaline medium. .6 per cent., .3 per cent. and .1 per cent. solutions of sodium carbonate were employed, experiments being tried with both starch and glycogen. 1 gram of peptones was used in each case, and as this amount was dissolved in 50 cc. of the dilute alkali, the digestive mixture of 100 cc. contained approximately one-half the percentage of alkali employed. The following results were obtained:

1. With .6 per cent. Na_2CO_3 and 1 gram peptones.

	Saliva alone. Wt. Cu in one-tenth.	*Saliva + 50 cc. Alkali.* Wt. Cu in one-tenth.	*Saliva, Alkali and Peptones.* Wt. Cu in one-tenth.
Starch	.0905 gram	.0239 gram	.0456 gram
"	.0904 "	.0222 "	.0486 "
"	.0835 "	.0214 "	.0515 "
Glycogen	.1300 "	.0312 "	.0683 "

2. With .3 per cent. Na_2CO_3 and 1 gram peptones.

	Saliva alone. Wt. Cu in one-tenth.	*Saliva + 50 cc. Alkali.* Wt. Cu in one-tenth.	*Saliva, Alkali and Peptones.* Wt. Cu in one-tenth.
Starch	.0904 gram	.0393 gram	.0685 gram
"	.0835 "	.0331 "	.0710 "
Glycogen	.1281 "	.0423 "	.1050 "

3. With .1 per cent. Na_2CO_3 and 1 gram peptones.

	Saliva alone. Wt. Cu in one-tenth.	*Saliva + 50 cc. Alkali.* Wt. Cu in one-tenth.	*Saliva, Alkali and Peptones.* Wt. Cu in one-tenth.
Glycogen	.1281 gram	.0908 gram	.1197 gram

It becomes evident then from these experiments that in a solution containing either .3 per cent. or .15 per cent. of sodium carbonate, the presence of the peptones nearly doubles (quite and even more in the case of glycogen) the diastatic action, bringing it up almost to the action of the unaltered saliva. It may be questionable whether these experiments afford proof positive that the peptones stimulate the pancreatic ferment in the conversion of starch into sugar in the intestinal canal, but it is certainly proven that under such conditions as have been described here, the presence of 1 per cent. of peptones in a .3 per cent. sodium carbonate solution causes a greatly increased formation of sugar. Thus it seems probable that in the proteid and diastatic pancreatic digestion the formation of peptones, which must go on side by side with the formation of sugar, affords a decided aid to the latter process.

We next endeavored to ascertain whether the salts already experimented with have any influence on diastatic action in alkaline solutions of the strength specified. The following experiments were tried:

First Experiment.

				Wt. Cu in one-tenth.	
Saliva and starch alone,				.0872	gram
“	“	+50 cc. .6 per cent. Na_2CO_3=.3 per cent. alkali		.0220	“
“	“	“	“ +.012 gram NaCl	.0287	“
“	“	“	“ +.012 “ Na_2HPO_4	.0275	“

Second Experiment.

				Wt. Cu in one-tenth.	
Saliva and starch alone,				.0844	gram
“	“	+50 cc. .6 per cent. Na_2CO_3=.3 per cent. alkali		.0225	“
“	“	“	“ +.015 gram $CaHPO_4$	.0211	“
“	“	+50 cc. .3 per ct. Na_2CO_3=.15 per cent. alkali		.0348	“
“	“	“	“ +.015 gram $CaHPO_4$	.0395	“

It is thus very evident that these salts have little or no influence on diastatic action, in alkaline solutions of the strength used. It next remained to try the influence of the ash of the peptones in alkaline solution. The ash of 1 gram of peptones was employed, the experiment being conducted in the same manner as the preceding. The peptones used were those with 1.71 per cent. of ash. Following are the results:

				Wt. Cu in one-tenth.	
Saliva and starch alone,				.0862	gram
“	“	+50 cc. .6 per cent. Na_2CO_3=.3 per cent. alkali		.0216	“
“	“	“	“ +ash 1 gram peptone	.0313	“
“	“	“	“ +1 gram peptone	.0520	“

Saliva and starch alone,	.0862	gram
" " + 50 cc. .3 per cent. Na_2CO_3 = .15 per cent. alkali	.0305	"
" " " " + ash 1 gram peptones	.0400	"
" " " " + 1 gram peptone	.0740	"

We therefore deem it safe to conclude that the inorganic salts contained in the peptones play but an unimportant part in the stimulating action noticed in an alkaline solution of the strength specified.

MARCH 20, 1882.

ON THE DETERMINATION OF REVERTED PHOSPHATES.[1]

BY THOMAS S. GLADDING.

In an investigation on the subject of reverted phosphoric acid, the first question that arises is, What is meant by this term? The curious phenomenon of a decrease in the amount of soluble phosphate in a superphosphate and its reversion into a form insoluble in water, but soluble in the organic salts of ammonia, in weak acids and other reagents, has been attributed to several different causes.

According to the most common explanation[2] it is due to the gradual interaction between the soluble or monocalcic phosphate formed in the manufacture, and the still undecomposed tricalcic phosphate of the original rock, this reaction resulting in the formation of the intermediate compound dicalcic phosphate.

Again, it has been noticed that this reversion is especially large when the amounts of iron and alumina present are considerable, and in such cases it has been attributed[3] to the formation of phosphates of iron and alumina having the solvent properties specified above.

Again, from experiments in our own laboratory it has been found that this reversion is very noticeable in acid phosphates, which, after treatment with sulphuric acid, have been mixed with natural phosphates containing large amounts of carbonate of lime. The reaction that takes place between the monocalcic phosphate and carbonate of lime probably results in the formation of either the dicalcic or tricalcic phosphate. This latter salt, though insoluble in water, is readily taken up, on account of its fine state of division, by the reagents used for the estimation of reverted phosphates.

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[1] Read before the American Chemical Society, March 17, 1882.

[2] Zeit. für analyt. Chem. **10**, Fresenius.

[3] Zeit. für analyt. Chem. **19**, Z. Meyer.

From these different explanations of the character of reverted phosphate it is evident that the term is not capable of a strict chemical definition. It may consist in any given case of one or of several chemical compounds. The best definition that can be given is the general one condensed into the name itself. Reverted phosphates are those which, originally insoluble, but having been made soluble, have reverted or returned to the insoluble condition. They must now, however, be looked upon as:

(1) Just over the border line that separates the soluble from the insoluble, lying very close to the soluble and being brought back by a slight addition to the solvent power of water; and, as

(2) Widely separated and different in solubility from the insoluble form which they originally possessed. Like the flats lying just above the river's edge, they must be wholly covered by a slight rise in the water that affects the banks but little.

The object of the inquiry here described has been to establish the above distinctions, and to find a method of separation that shall in the actual analysis recognise them as nearly as possible. The course pursued has been that followed in similar inquiries:

I. An examination of the solubility of the different natural phosphates used in the manufacture of superphosphates.

II. An examination of the solubility of the different chemical compounds of which reverted phosphates have been found to consist; and

III. An attempt based upon the results of these two inquiries to find the best method of separating these two classes.

In the examination of the natural phosphates, five different forms were taken as typical of all. These were:

1. *Apatite*, as type of the nearly pure tricalcic form in its most insoluble condition.

2. *South Carolina rock*, containing besides tricalcic phosphate, phosphates of iron and alumina, and carbonate of lime.

3. *Bone Ash*, the great organic source of phosphate.

4. *Navassa rock*, typical on account of its large percentage of iron and alumina; and finally,

5. *Curaçao phosphate*, as type of the island phosphates, notable for their peculiar mechanical condition and greater solubility in the organic salts of ammonia.

In examining the solubility of these natural phosphates, attention was first given to the effect of different relative proportions of phosphate and solvent. The standard method of Fresenius, Luck and Neubauer[1] was followed, using 50 cc. of citrate of ammonia solution, of sp. gr. 1.09, and made as nearly neutral as possible, time 30 minutes, temp. 35° C. Two series of experiments were made. In the first, one gram of substance was taken; in the second, $\frac{1}{10}$ of a gram.

	SERIES I.	SERIES II.
	P_2O_5 dissolved.	P_2O_5 dissolved.
Apatite	0.40 per cent.	1.54 per cent.
South Carolina rock	2.00 "	6.60 "
Bone Ash	2.60 "	8.30 "
Navassa	2.65 "	10.10 "
Curaçao	4.40 "	16.00 "

Comparing these tables, we see at once the fact that has been commented upon very frequently of late by German chemists as regards superphosphates, and to which special attention has been called within a few months by a printed letter of Dr. S. W. Johnson, in the case of Curaçao phosphate, namely, that the percentage of phosphate dissolved increases very largely with the increase of solvent, or, what is the same, the decrease of substance taken for analysis. These tables show that this is true not only of reverted phosphates as found by the former, nor of Curaçao phosphate as shown by the latter, but also of all natural phosphates, including even the difficultly soluble apatite. This fact has a very important bearing upon the error involved in the determination of reverted phosphoric acid by this method, *i. e.* an error as regards the strict separation of the reverted phosphates from the insoluble phosphates. Thus, supposing five superphosphates after the extraction of the soluble to contain no reverted phosphate, but to contain 10 per cent. of the above raw phosphates respectively, corresponding to about 3 per cent. of insoluble phosphoric acid, the citrate would attack these raw phosphates, and instead of the error being

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[1] Zeit. für analyt. Chem. **10.**

0.04, 0.20, 0.26, 0.26 and 0.44 per cent. as would naturally be supposed from Series I., it would in reality be 0.15, 0.66, 0.83, 1.01 and 1.60 per cent. as shown by Series II. Thus, the superphosphates would be reported as containing these latter amounts of reverted phosphoric acid, when in fact they contained none whatever.

This same fact of increased solvent power obtained by increasing the amount of solvent salt was shown to be true also of oxalate of ammonia, by treating 2 grams of Navassa rock and Curaçao phosphate with 1, 5, and 10 grams of the salt dissolved in 100 cc. of water, at a temperature of 100° C. for 30 minutes.

SERIES III.

	1 gram.	5 grams.	10 grams.
Navassa, P_2O_5 dis.,	2.20	8.75	12.15
Curaçao, " "	2.50	12.30	17.60

The influence of increase of temperature upon the amount of rock dissolved was shown by treating one gram of the different phosphates with 100 cc. of water containing four grams of oxalate at 20°C. and at 100°C.

SERIES IV.

	Apatite.	So. Car. Rock.	Bone Ash.	Navassa.	Curaçao.
At 20°C. P_2O_5 dis.	0.36 per ct.	2.25 per ct.	2.72 per ct.	2.85 per ct.	5.51 per ct.
" 100° " "	2.16 "	5.80 "	8.78 "	9.40 "	15.30 "

In performing the above experiments at 100°C. a strong odor of evolved ammonia was observed, and it was also found that the filtrates were decidedly acid in reaction. The importance of this and its bearing upon the subject will be better seen further on.

The results thus far given show very clearly the cause of much of the confusion that has arisen over the determination of reverted phosphates. This lies in the great facility with which the citrate and oxalate solutions attack the insoluble phosphate, especially when the proportion of solvent is increased or when the temperature of digestion is raised. Many chemists have been led by these difficulties to seek a better method. The suggestion has frequently been made that a weak or dilute acid be employed as a substitute for the organic salts of ammonia. Thus Grupe and Tollens[1] recommend the use of a ¼ per cent. citric acid solution. The solvent power of this acid of ¼ per cent., also of oxalic acid of ¼ per cent. and $\frac{1}{10}$ per cent., also of hydrochloric acid of $\frac{1}{100}$ normal strength, upon the natural phosphates was examined. 100 cc. of each of the above solvents were taken, the temperature of digestion was 40°C., time one hour. One gram was taken with each acid, and in addition also $\frac{1}{10}$ of a gram with the citric acid of ¼ per cent.

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[1] Berichte der deutsch. chem. Gesellschaft, **14**, 754.

SERIES V.

Acid employed—		Citric ¼ per ct.		Oxalic ¼ per ct.	Oxalic $\frac{1}{10}$ per ct.	HCl $\frac{1}{100}$ normal.
		1 gram.	$\frac{1}{10}$ gram.	1 gram.	1 gram.	1 gram.
Apatite,	P_2O_5 dis.	0.74 per ct.	2.70 per ct.	3.20 per ct.	1.08 per ct.	2.56 per ct.
So. Car. rock,	"	2.80 "	11.40 "	8.75 "	2.68 "	4.25 "
Bone Ash,	"	3.80 "	11.80 "	9.23 "	4.15 "	3.85 "
Navassa,	"	3.30 "	14.00 "	9.96 "	3.50 "	4.15 "
Curaçao,	"	4.20 "	19.80 "	9.12 "	4.00 "	3.35 "

Supposing a fertilizer to contain 10 per cent. of insoluble rock, the citric acid would make the reverted phosphoric acid 0.27 per cent., 1.14 per cent., 1.18 per cent., 1.40 per cent., 1.98 per cent. respectively in excess of the actual amount present. The excess thus introduced would be considerably greater than that caused by the solvent action of the citrate of ammonia solution, *vide* Series II., and the claim made for the citric acid solution by Grupe and Tollens that it dissolves nearly the same amount of phosphate from different quantities of substance taken for analysis shown to be wholly unfounded as regards its action on raw phosphates. (Compare columns 1 and 2 above.)

The action of the different solvents upon the dicalcic and tricalcic salts was next studied. These salts were obtained by precipitation, and on analysis found to agree so closely with the theoretical composition as to show the admixture of traces only of other forms. After thorough washing they were mixed with about an equal weight of calcium sulphate, in order to imitate the conditions under which they are found in a superphosphate. These mixtures were then thoroughly air-dried. One gram of each was now treated with the different solvents, already employed, for 30 minutes at a temperature of 40°C. The mixture of the dicalcic salt contained 19.20 per cent. of P_2O_5, of the tricalcic salt 13.00 per cent.

SERIES VI.

Solvent.		$2CaOP_2O_5$.		$3CaOP_2O_5$.	
160 cc. ¼ per cent. citric acid,	P_2O_5 dis.=	10.60 9.31	per cent.	10.26	per cent.
100 cc. $\frac{1}{10}$ " oxalic acid,	"	5.32	"	5.10	"
" 1 normal HCl "	"	3.42	"	1.90	"
50 cc. cit. of ammonia sol.	"	19.20	"	13.00	"
50 cc. H_2O+1 gram oxal. ammo.	"	19.00 19.05	"	11.50	"

It will be seen from this table that the citrate solution dissolves both forms perfectly; that the citric acid, though fairly successful with the tricalcic salt, dissolves only one-half of the dicalcic salt; that the other acids, notably the mineral acid HCl, fall far below the citric in this respect. Special attention is called to the vigor of the weak solution of oxalate of ammonia. Though only one gram is used, it dissolves all but a trace of the dicalcic salt, and falls but little short of dissolving all the tricalcic form. In the original article of Fresenius, Luck and Neubauer, the weak acids were discarded an account of their inability to take up the reverted phosphate. This conclusion is corroborated by these experiments, with the additional objection proved by Series V., namely, the greater extent to which they dissolve the insoluble phosphate. They found also that oxalate of ammonia solution dissolved the dicalcic phosphate equally with the citrate salt, but abandoned its use on account of the vigor with which it attacked the raw phosphates. But they employed in their published experiments a very large amount of oxalate, six grams of the salt being taken. But it is here found that a much weaker solution of the oxalate is effective for dissolving the dicalcic salt. As to its solvent action upon the natural phosphates, a series of experiments proved that it was not as energetic in this respect as the citrate of ammonia solution, dissolving considerably less than the latter. On account of the many advantages possessed by an oxalate of ammonia solution over the citrate solution (1) as regards ease of preparing a perfectly uniform, neutral solution, (2) as to the greater facility of filtering and washing, and many others, many chemists urged and secured its adoption at the Cincinnati convention of agricultural chemists of 1881. But further experiments, to be described later, reluctantly compelled the conclusion that it cannot supersede the citrate of ammonia solution.

A series of experiments were now made upon a sample of acid phosphate, in order to compare the results obtained by the different methods, and to throw light, if possible, upon the causes of discrepancy. A sample made from Navassa rock was chosen on account of the large amount of reverted phosphate usually present in this class of fertilizers. The total phosphoric acid in the sample was 17.00 per cent., the soluble was 5.00 per cent., leaving 12.00 per cent. of reverted and insoluble. After thoroughly washing out the soluble, one gram was treated with 50 cc. of citrate of ammonia solution, and the directions of Fresenius carefully followed. Another gram was treated in exactly the same way, using however as a solvent 50 cc. of water containing in solution one gram of oxalate of ammonia. The following results were obtained:

SERIES VII.

	P_2O_5 dissolved.	P_2O_5 undissolved.
By citrate solution or "Washington method,"	6.10 per cent.	5.90 per cent.
By oxalate solution,	6.15 "	5.85 "

These two methods give results that are gratifying as regards their agreement. Subsequent experiments, however, showed conclusively that both were far from the truth.

Two grams of the same sample were now, after the extraction of the soluble phosphate, treated according to the method adopted by the agricultural chemists at Cincinnati, known as the "Cincinnati method." The two grams of residue were washed from the filter paper into a beaker with 100 cc. of water, containing in solution two grams of oxalate of ammonia. (This is the same amount of oxalate in proportion to the quantity of substance taken as is used in the above determination.) 400 cc. of water are brought to boiling, and the beaker closely covered now introduced in the boiling water, the lamp being at the same time removed. The temperature of the liquid in the beaker will rise to about 70° C. in a few minutes, and will then slowly sink during an hour to about 40° C. The beaker is briskly rotated at intervals. Two grams were treated in exactly the same manner, using, however, instead of the oxalate solution 100 cc. of the citrate solution.

SERIES VIII.

	P_2O_5 dissolved.	P_2O_5 undissolved.
By oxalate of ammonia	8.55 per cent.	3.45 per cent.
" citrate "	9.85 "	2.15 "

The point of interest connected with these results is the much larger amount of phosphoric acid dissolved by both the reagents as compared with that dissolved by them at the temperature of 35°C. continuous. This is especially the case with the citrate solution, the dissolved phosphoric acid rising from 6.10 per cent. to 9.85 per cent., an increase of 3.75 per cent. This increase can be explained in two ways only: (1) Either the insoluble rock present is dissolved to this increased extent, or (2) there is a form of reverted phosphate present that is not fully taken up by either the citrate or oxalate solution at the lower temperature.

In order to ascertain if the former of these two explanations was the correct one, two separate portions of $\frac{3}{8}$ of a gram each of Navassa rock containing 0.120 gram P_2O_5, and corresponding to 6 per cent. of insoluble phosphoric acid when calculated on two grams as used in the above analysis (which is just the amount of apparently insoluble acid left in Series VII.), were rubbed to a paste in a mortar and treated each with 100 cc. of citrate of ammonia solution, the one at a temperature of 35°C. continuous for one hour, the other at a temperature falling from 70°C. to 40°C. during an hour, as in Series VIII. The following amounts of P_2O_5 were dissolved, calculated as per cent. on 2 grams:

SERIES IX.

No. 1.	Phos. acid dissolved,	1.16 per cent.
No. 2.	" " "	1.59 "

The increase in phosphoric acid dissolved by the use of the higher temperature is found to be only 0.43 per cent. It is seen at once that this small increase cannot explain the large increase of 3.75 per cent. in the case of the acid Navassa, made from the same rock.

The second of the two possible explanations, viz. the presence of a form of reverted phosphate not fully dissolved at 35°C., must therefore be the true one. The experiments already made show that this form can be neither the dicalcic nor tricalcic phosphates, as the citrate solution is a perfect solvent for these two forms at a temperature of 35°C. The only form left is the reverted phosphate of iron and alumina. A quantity of the mixed normal phosphates of iron and alumina, Fe_2O_3, P_2O_5 and Al_2O_3, P_2O_5, was now prepared by precipitation. A portion was mixed with a large quantity of calcium sulphate and dried to a powder at a temperature not exceeding 60°C. The remainder was dried at the same temperature without admixture. One gram of the first portion containing 4 per cent. of phosphoric acid was now rubbed to a paste in a mortar and then digested with 100 cc. of the oxalate and citrate solutions, first at 35°C. and then at 70°C. to 40°C. for one hour.

SERIES X.

	P_2O_5 dis. at 35°C.	P_2O_5 dis. at 70° to 40°C.
Using oxalate of ammonia,	0.95 per cent.	3.20 per cent.
" citrate "	1.60 "	4.00 "

One gram of the unmixed portion containing on analysis 35.62 per cent. of phosphoric acid was now treated exactly in the same way, with results as follows :

SERIES XI.

	P_2O_5 dis. at 35°C.	P_2O_5 dis. at 70° to 40°C.
Using oxalate of ammonia	11.06 per cent.	26.50 per cent.
" citrate "	13.14 "	35.62 "

These two series of experiments prove the very important fact that neither the citrate nor oxalate solution will dissolve more than a small portion of the reverted phosphates of iron and alumina at the temperature of 35° C., and that even at the higher temperature of 70° C. to 40° C. the oxalate falls short of the perfect solvent power which must be required of it.

These results explain most clearly the great increase of phosphoric acid taken up in Series VIII. over that dissolved in Series VII. The acid Navassa under treatment contains a very large quantity of reverted phosphates of iron and alumina which are not dissolved at the lower temperature. They also explain why the citrate solution dissolves 1.30 per cent. more than the oxalate, because of its more vigorous solvent action on these forms of reverted phosphates. One gram of these phosphates of iron and alumina, treated with

100 cc. of the citrate solution at a continuous temperature of 65° C. for 30 minutes, formed also a clear solution.

In order to ascertain the amount of solvent action of this method upon the different forms of raw phosphates, ⅕ of a gram of each, corresponding to about 3 to 4 per cent. phosphoric acid when calculated upon two grams, was treated in the same manner as the above, temperature 70° C. to 40° C., using 100 cc. citrate solution.

SERIES XII.

	P_2O_5 dis.
Apatite	0.22 per cent.
South Carolina rock	0.61 "
Bone Ash	...
Navassa rock	1.09 "
Curaçao	2.07 "

Comparing this table with Series II., dividing the results there by ten, it is evident that at the higher temperature, only a small increase in the amount of insoluble rock dissolved is observed.

In this connection special attention is called to one point. Notice has been called to the fact that at 100° C. the oxalate solution loses ammonia and becomes decidedly acid in reaction. A solution of neutral oxalate, immersed in boiling water for one hour in an open beaker, acquired an acid strength of ⅕ per cent. oxalic acid; 100 cc. of the citrate of ammonia solution treated for an hour in the same way acquired an acid strength of 1.2 per cent. citric acid. The energy with which these acid solutions attack the undecomposed rock present in a superphosphate is shown in Series V. It is on account of these facts that Fresenius uses a neutral solution of the citrate salt and adopts the low temperature of 35° C., and Luck[1] in a second paper dwells with great emphasis upon this point in answer to the criticisms of a French chemist. But as the higher temperature is rendered indispensable on account of the presence of phosphates of iron and alumina in the great majority of superphosphates, this loss of ammonia and consequent acidity was prevented by digestion in a flask closed with a rubber cork.

The severest criticism upon the determination of reverted phosphates as an analytical process is the fact that when different quantities of substance are taken for analysis, different results are obtained. This most exceptional experience in chemical analysis, which is without a parallel in analytical determinations, requires a most careful examination, as this has done more than all else to cast discredit upon this analytical process. And yet it seems clear that this trouble can arise from only three sources:

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[1] Zeitschrift für anal. Chem. **14.**

(1) Either the fertilizer under treatment has so large an amount of reverted phosphate present that when a large amount is taken for analysis the citrate is unable to take it all up, but is able to do so when a smaller amount is employed, or—

(2) The citrate is an imperfect solvent for some form of reverted phosphate that may be present, either on account of the character of the latter, or on account of the method employed failing to dissolve it completely, the error showing more clearly as larger quantities are taken for the analysis, or—

(3) The discrepancy arises from the solvent action of the citrate upon the undecomposed rock present, a larger percentage of this being dissolved when smaller quantities are taken (*vide* Series I. and II.). The instances given by German experimenters, in the case of fertilizers containing 25 per cent. or more of phosphoric acid present as precipitated tricalcic phosphate, may be due mainly to the first of these causes. In such cases a smaller quantity must be taken, or it may be found that the higher temperature here recommended will so increase the solvent power of the citrate solution as to render this unnecessary. Whenever the phosphates of iron or alumina are present, it is evident from the experiments given that this discrepancy may be largely due to the second cause here assigned, namely, the method of the analysis, employing as it does the low temperature of 35° C. In order to ascertain whether the higher temperature of 70° C. to 40° C. will obviate the error from this second cause, 1, 2, 3, 4, and 5 grams of the above acid Navassa were treated each with 100 cc. of the citrate solution at this temperature, after the thorough washing out of the soluble phosphate.

SERIES XIII.

	P_2O_5 dissolved.	P_2O_5 undissolved.
Employing 1 gram substance	10.06 per cent.	1.94 per cent.
" 2 "	9.85 "	2.15 "
" 3 "	9.65 "	2.35 "
" 4 "	9.43 "	2.57 "
" 5 "	9.02 "	2.98 "

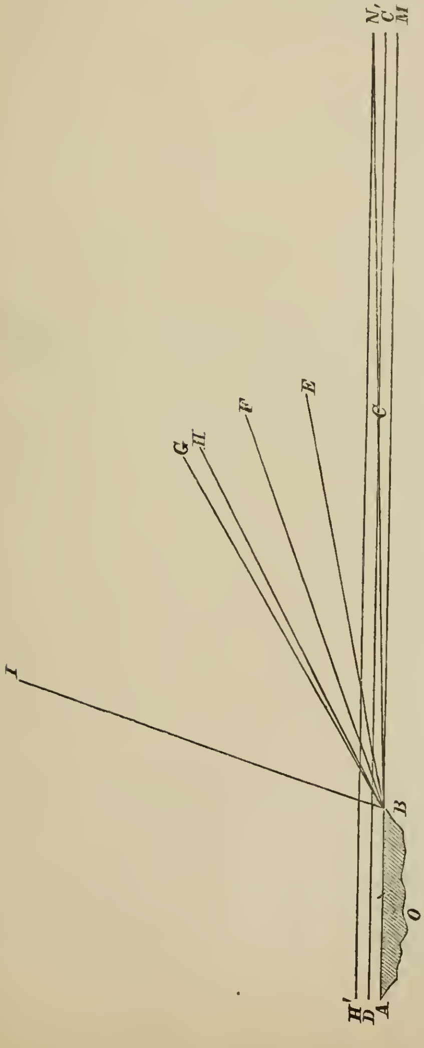
The very slight and uniform decrease of reverted phosphoric acid, about 0.20 per cent. for each additional gram taken, up to the 5 grams when the increase is a trifle larger, would certainly seem to show that every source of discrepancy but the third mentioned above had been obviated. When it is observed that in the last experiment 0.451 gram of reverted phosphoric acid is dissolved by the 100 cc. of citrate of ammonia solution at the temperature of 70° C. to 40° C., it certainly seems that nothing further could be desired as regards vigor of action upon the reverted forms. No other solvent suggested will approach the citrate solution in this important respect, when employed at the temperature here adopted.

But as regards the third cause of discrepancy it is very different. This cause lies in the very nature of things and cannot be overcome. No reagent can be found that will dissolve the strictly reverted phosphates and not affect the undecomposed rock present. Nor is it desirable that any such reagent should be found, nor would it be just to employ it in case it were possible to find it. The whole idea upon which the determination of reverted phosphates rests is that the solvent action of the liquids of the soil is stronger than that of pure water, and is closely imitated by the solvent action of the organic salts of ammonia. Now there is a certain percentage of the raw phosphates that will always be taken up by this increased solvent power, and this percentage is practically and with justice considered equal in value to and reported as reverted phosphate.

The only difficulty that now presents itself is to so fix the amount of substance taken for analysis that the solvent action of the citrate solution upon the undecomposed rock shall dissolve such a percentage of this as shall when reported as reverted phosphate be a fair equivalent of its agricultural value. This conception here stated will be best illustrated by the accompanying diagram. 2 grams of the five forms of raw phosphates were treated with 100 cc. of citrate of ammonia solution at a falling temperature 70° C. to 40° C. for one hour, also two grams of the reverted phosphates of iron and alumina containing 35.62 per cent. of phosphoric acid. The latter was dissolved to a clear solution.

SERIES XIV.

Apatite,	Phosphoric acid dissolved,		0.60	per cent.
South Carolina rock,	"	"	2.62	"
Bone Ash,	"	"	3.15	"
Navassa,	"	"	3.75	"
Curaçao,	"	"	7.50	"
Reverted phos. of iron and alumina,	"	"	35.62	"



In the diagram use is again made of the figure of speech previously employed. AOB is the river bed, representing the phosphates soluble in water, completely covered by the line AM, the height of which represents the solvent power of water. The line BC represents the flats or the reverted phosphates lying just above the water, and slightly rising, since the different forms possess different degrees of solubility. The line DC′ represents the solvent power of 100 cc. of citrate of ammonia solution at the temperature 70° C. to 40° C. The lines BE, BF, BH, BG and BI represent the banks rising at different angles, or the different raw phosphates, Curaçao, Navassa, Bone Ash, South Carolina rock, and Apatite here examined. These lines are all two inches in length, to represent the two grams of substance taken. All of BC falls below DC or becomes soluble in the citrate solution, $\frac{1}{4}$ of BE, $\frac{1}{8}$ of BF, $\frac{1}{11}$ of BH, $\frac{1}{10}$ of BG, and $\frac{1}{70}$ of BI, calculating from 30, 30, 36, 27, and 42 percentages of phosphoric acid present in the five samples.

Now suppose one gram of the above substances be taken to 100 cc. of citrate solution. This proportion is the same as 200 cc. citrate solution to the 2 grams of substance taken in the diagram. The line DC will be raised to H′N, twice as far above the surface of the water. Twice as large an amount of reverted phosphates will be taken up, viz. BN, and at the same time nearly twice as large an amount of the raw phosphates as shown in the figure. Thus repeating Series XIV., using however one gram of substance, there were dissolved as follows:

SERIES XV.

Apatite,	Phosphoric acid dissolved,	1.06 per cent.
South Carolina rock,	" "	...
Bone Ash,	" "	5.20 "
Navassa,	" "	6.20 "
Curaçao,	" "	11.50 "

Attention is called to the nature of Curaçao phosphate as brought out in this connection. Since by successive treatments with citrate of ammonia solution, or by employing a very small quantity for analysis, as $\frac{1}{10}$ of a gram, nearly all of this can be brought into solution, many chemists regard its phosphoric acid as nearly all in the available form, and an analysis made by one chemist on the identical sample used in this work reports the presence of 18 per cent. of reverted phosphoric acid. But the whole course of experiments given in this paper shows conclusively that it differs from the other raw phosphates only in degree of solubility, and is very far removed as regards this property from the true reverted forms, being, as shown in the diagram, based upon Series XIV., only $\frac{1}{5}$ as soluble at the best as the latter, and only about twice as soluble as Navassa rock and bone ash.

It seems almost certain from the agricultural experiments described in the last edition of Johnston's "Agricultural Chemistry," on the use of finely ground raw phosphates, that all the phosphoric acid in such phosphates becomes ultimately soluble in the soil. The division of phosphates therefore into the three forms, soluble, reverted, and insoluble, will have reference only to the time required to render them available for plant use. Supposing, in the above diagram, that the solvent action of 100 cc. of the citrate solution represents the solvent action of the liquids of the soil for a certain period of time, as *e. g.* one season, upon the forms of phosphate there represented, it is evident that all the soluble and reverted would be available the first season, that raw Curaçao would all be rendered available in something over five seasons, the Navassa in eight seasons, and so on. The divisions, therefore, of soluble, reverted, and insoluble become indispensable as means of fixing commercial and agriculturnl values.

In conclusion, emphasis is laid upon the following points as brought out in this inquiry:

I. While the line of division between the reverted forms and the original insoluble forms of phosphoric acid may be sharply drawn in the case of an extremely insoluble phosphate, like apatite, in the case of the more easily soluble natural phosphates the two great classes overlap, one the other. Whatever solvent therefore is used for determining reverted phosphates, the same will also dissolve a small percentage of the undecomposed phosphate that may be present; this percentage varying considerably according to the character of the insoluble phosphate. This percentage, representing as it does the comparative solubility which such insoluble phosphate possesses to the true reverted phosphates present, is justly considered as equivalent to an equal amount of the true reverted forms, and reported as such.

II. A slightly ammoniacal citrate of ammonia solution, alone of all the solvents that have been proposed, is a perfect solvent for all the forms of reverted phosphate, while at the same time not unduly dissolving the raw or insoluble phosphates present. Such a solution dissolves but a trace of the most difficultly soluble form of phosphate known, viz. apatite, and dissolves the other natural phosphates to a greater and greater extent as they approach in character the true reverted forms.

III. Neither the "Washington method" (method of Fresenius) nor the "Cincinnati method" can be relied upon to take up all the reverted phosphates that may be present.

IV. A modification of the method of Fresenius, consisting of the use of a higher temperature for the digestion, will meet all the requirements of the case, provided that the greatest care is taken to guard against acidity of the solvent and consequent excessive solution of the insoluble phosphates present. Whether the falling temperature of 70° C. to 40° C. as here explained, or a continuous temperature of 65° C. for 30 minutes, be used, there will be but slight if any differences in the results, provided that the solution of citrate be slightly ammoniacal, and the digestion be made in a closed flask. To the use of *acid* solutions of citrate, either acid at the beginning of the digestion or becoming acid during its continuance, are probably due, more than to any other cause, the discrepancies in this analytical process.

LABORATORY OF STILLWELL AND GLADDING, NEW YORK.

COLUMBITE, ORTHITE AND MONAZITE FROM AMELIA CO., VIRGINIA.

BY F. P. DUNNINGTON.

Among the minerals found with microlite (see Vol. 3, No. 2, of this Journal) one variety of columbite attracted attention by its decided red color when in thin splinters. It proved to have the following properties: Hardness, 5.5; specific gravity, 6.48; lustre, sub-resinous; color, dark brown; streak, light brown.

Analysis gave the following results:

Ta_2O_5, Nb_2O_5, SnO_2—trace	84.81
MnO,	8.05
FeO,	5.07
CaO,	1.27
MgO,	.20
Y_2O_3(?)	.82
	100.22

The excess of the manganese over the iron is peculiar, and probably accounts for the unusual red color of the splinters and light color of streak.

The specific gravity of the mixed acids = 6.51. Pure Ta_2O_5 and Nb_2O_5 similarly ignited respectively gave the specific gravities 7.87 and 4.20, from which data we obtain an approximate estimation of the amounts of the acids:

Ta_2O_5, 53.4, and Nb_2O_5, 31.4 per cent.

The oxygen ratio for the metallic acids and the bases will then be:

$$Ta : Nb : R = 27 : 26 : 10,$$

thus affording a formula in which the molecular ratio of Nb_2O_5 to $Ta_2O_5 = 1 : 1$.

In Dana's Mineralogy there have been observed the ratios:

$$Nb_2O_5 : Ta_2O_5 = 2 : 1, 3 : 1 \text{ and } 4 : 1.$$

As may have been expected from the above analysis, the specific gravity of this mineral is greater than that of any of the specimens whose analyses are quoted by Prof. Dana.

Orthite also is found in this locality. It occurs in blade-like crystals several inches in length; the faces of the crystals being partly decomposed, no accurate measurements of the angles could be made. Hardness, 5.5; specific gravity, 3.323; lustre, pitchy; color, greyish black; streak, greenish grey. It fuses with much intumescence, and is gelatinized by hydrochloric acid without applying heat. Analysis gave the following:

SiO_2,	32.35
Al_2O_3,	16.42
Fe_2O_3,	4.49
Ce_2O_3,	11.14
La_2O_3,	3.47
Di_2O_3,	6.91
FeO,	10.48
MnO,	1.12
CaO,	11.47
K_2O, Na_2O,	.46
H_2O,	2.31
	100.62

Monazite also is found in this locality. It was first identified by Dr. G. F. Koenig, who published a notice of it in the Proceedings of the Academy of Natural Sciences of Philadelphia, Jan. 24, 1882.

Before seeing this notice, I made an analysis of a specimen of the mineral in question, and as this shows the presence of thorina, not before noticed, I give my results:

Ce_2O_3	16.30
Di_2O_3	24.4
La_2O_3	10.3
Y_2O_3	1.1
Fe_2O_3	.9
Al_2O_3	.04
[1] ThO_2	18.6
P_2O_5	24.04
SiO_2	2.7
	98.38

If we exclude the thorina and silica, we shall have for the remaining constituents, approximately, the formula $R_2'''P_2O_8$; hence it is possible that the thorina may occur in the form of orangite, but the analysis has not been made with sufficient accuracy to decide this point.

UNIVERSITY OF VIRGINIA, *March*, 1882.

Laboratory Notes from the University of Cincinnati.

XXVI.—A NEW MINERAL FROM COLORADO.

BY F. W. CLARKE AND N. W. PERRY.

A few months ago one of us received from an assayer at Gunnison city a peculiar mineral which had been brought in for examination from a point about twenty miles to the southward of that place. It was said to exist in considerable quantity, and information was sought as to its probable value; but no details as to its mode of occurrence or associations were given.

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[1] Sp. grav. = 7.5; hence not pure.

The mineral is massive, easily scratched by the knife, and deep purple in color. In powder the purple tint is retained. At first sight it suggests yttrocerite, a fact which led us to immediately examine it for fluorine. It is associated with a semi-massive calcite, which in portions is tinged with ferric oxide. Although the mineral forms a distinct layer upon the calcite more than a centimetre in thickness, it is so penetrated by the latter species that we could not effect a complete mechanical separation of the two substances. Hence a correction for admixed calcite has to be applied to the results of actual analysis. Sp. gr. 2.85.

The analysis was made under our direction, by Mr. E. A. Kebler, with the following results:

Fluorine,	31.96
Calcium,	45.91
Silica,	6.02
Alumina, (+ tr. Fe_2O_3),	5.21
Carbon dioxide,	5.61
Soda,	.74
	93.45

The loss is oxygen, which should be reckoned as united with a part of the calcium. A second fluorine estimation gave 31.86 per cent. Assuming that the fluorine and carbonic acid are wholly united with calcium, and recalculating the remainder of the calcium as oxide, the foregoing results may be stated as follows:

CaF_2,	65.60
$CaCO_3$,	12.75
CaO,	10.02
SiO_2,	6.02
Al_2O_3,	5.21
Na_2O,	.74
	100.34

If we regard the calcium carbonate as being merely admixed calcite, and recalculate the balance of the analysis, we have for the mineral the following composition:

CaF_2,	74.89
CaO,	11.44
SiO_2,	6.87
Al_2O_3	5.95
Na_2O,	.85
	100.00

These figures agree very closely with the following formula:

$$7CaO.2Al_2O_3.4SiO_2.32CaF_2.$$

Possibly an analysis of purer material might give the simpler ratio:

$$4CaO.Al_2O_3.2SiO_2.16CaF_2.$$

Whether or no the mineral is a definite and distinct species can be determined only by additional investigation. The locality at which it was found ought to be carefully studied, and the associated minerals examined. Probably the mineral is an alteration product of fluor spar, although it may be only a mixture of that species with a silicate. Still, with the exception of the admixed calcite, the mineral seems to be homogeneous, and the color of its powder is unlike that of fluorite. If it should finally be established as a new species we shall propose for it the name of gunnisonite.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

By Ira Remsen.

XI.—OXIDATION OF METATOLUENESULPHAMIDE.

By Chase Palmer.

It has been shown in earlier papers of this series that oxidizable groups situated in the meta-position relatively to negative groups in benzene are converted into carboxyl, apparently with the same readiness as similar groups in the para-position. In the cases described, however, the influence of the negative groups has been, to some extent, concealed by the presence of ortho-groups. As it is established with a fair degree of certainty that acid oxidizing gents tend to transform para-groups and leave ortho-groups nchanged, and that alkaline oxidizing agents tend to transform rtho-groups and leave para-groups unchanged, it remains to be etermined whether meta-groups more closely resemble those in he ortho- or those in the para-position with respect to their conuct under the influence of oxidizing agents.

For the purpose of this study the amide of metatoluenesulphonic cid was selected. The acid was prepared according to the direcions given by Hübner and Müller,[1] by introducing a sulpho-group nto orthobromtoluene, and then substituting hydrogen for bromine n the product. One part of orthobromtoluene (obtained from ahlbaum and still containing some of the para-compound) was dded gradually to three parts of fuming sulphuric acid. The alcium salt of the sulphonic acid was converted into the sodium alt. The solution of the latter was kept in contact with weak odium amalgam for ten days, fresh amalgam being added as soon s the evolution of hydrogen stopped. The organic salt in soluion was then found to be free from bromine. The solution was eutralized with sulphuric acid and concentrated, when a large uantity of sodium sulphate crystallized out. After as much as ossible of the inorganic salts had been removed, the last mother iquor was evaporated to dryness. The dried residue was treated ith phosphorus pentachloride, and the chloride thus formed boiled ith concentrated aqueous ammonia. The sulphamide was exracted with ether and purified by repeated recrystallizations from ater. The product contained a not inconsiderable quantity of rtho-toluenesulphamide, the presence of which is readily accounted r by the fact that the bromtoluene used in the experiment ontained some of the para-compound. When sulphuric acid acts pon para-bromtoluene, the product formed contains the sulphoroup in the ortho-position relatively to the methyl, so that when he bromine is removed the product must be ortho-toluenesulhamide. The meta-amide, after purification, had the properties scribed to it by Hübner and Müller,[2] its fusing point being 90°–91°.

Conduct towards Potassium Permanganate.

To determine the influence of an oxidizing agent in alkaline soluons, a mixture was made consisting of five grams of pure metatoluenesulphamide and twenty grams potassium permanganate dissolved in five hundred cubic centimeters of water. The solution was made slightly alkaline. The whole was heated on a water bath for about twenty hours before the action ceased. When no further action seemed to take place, the slight excess of permanganate was reduced by means of a few drops of an aqueous solution of sulphur dioxide. The precipitated manganese hydroxides were filtered off, and the filtrate acidified with hydrochloric acid. On cooling an acid crystallized out in scales. The substance was purified by two or three crystallizations from hot water. It fused at 235° (uncorrected), at the same time suffering partial decomposition. It was converted into the barium salt by boiling the solution with barium carbonate. The salt crystallized from the concentrated solution. Dried over sulphuric acid its analysis gave results as follows:

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[1] Zeitschrift für Chemie, 1870, 449; 1871, 14; and Annalen der Chemie, **169**, 47.

[2] *Loc. cit.*

0.4728 gram salt lost 0.0557 gram H_2O at 120°, and gave 0.1776 gram $BaSO_4$=0.1044 gram Ba.

	Calculated for $\left(C_6H_4\left\{\begin{matrix}SO_2NH_2\\CO_2\end{matrix}\right.\right)_2Ba+4H_2O$.			Found.
$(C_7H_6SO_4N)_2$	400	65.69	...	...
Ba	137	22.49	...	22.08
$4H_2O$	72	11.82	...	11.78

The acid thus formed is identical with that described under the name of sulphobenzamic acid by Limpricht and Uslar,[1] and later by Engelhardt.[2] The former obtained it by heating sulphobenzamide, $C_6H_4\left\{\begin{matrix}SO_2NH_2\\CONH_2,\end{matrix}\right.$ or ammonium ethylsulphobenzoate with potassium hydroxide; and by treating the compound $C_7N_2H_6SO_2$ (obtained from sulphobenzamide by treatment with phosphorus pentachloride) with potassium hydroxide. Engelhardt obtained the acid by treating benzonitrile with sulphur trioxide. The identity of our product with "sulphobenzamic" acid was proved by comparing it directly with the acid prepared according to the method of Limpricht and Uslar. No difference was observed between them. The method of formation above described shows clearly that the substance is *metasulphaminebenzoic acid*, $C_6H_4\left\{\begin{matrix}SO_2NH_2\\CO_2H.\end{matrix}\right.$ The name sulphobenzamic acid is incorrect, as it applies only to a substance in which the amide group is in the carboxyl, viz. $C_6H_4\left\{\begin{matrix}SO_2OH\\CONH_2.\end{matrix}\right.$

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[1] Annalen der Chemie, **106**, 27.

[2] Journal für praktische Chemie, **75**, 363.

The principal feature of interest to be noted in the oxidation experiment is the fact that the action does not take place readily. The oxidation of ortho-toluenesulphamide with permanganate takes place very easily, that of the para-amide with difficulty. As nearly as could be judged the oxidation of a given quantity of the meta-amide required about the same time as the same quantity of he para-amide under the same conditions of temperature and dilu-ion, and a much longer time than the ortho-amide.

Conduct towards Chromic Acid.

The mixture used consisted of five grams of pure meta-oluenesulphamide, fifteen grams of potassium pyrochromate, and wenty grams of concentrated sulphuric acid diluted with three imes its volume of water. The flask containing the mixture was heated on a water-bath for about an hour, when the action was found to be complete. A crystallized product appeared in the mixture. After diluting with water and cooling, the acid formed was filtered off and purified by crystallization from water. As was expected, the product was identical with the meta-sulphamine-benzoic acid described above. The barium salt was made and analyzed.

0.339 gram of the salt lost 0.0383 gram H_2O at 120°, and gave 0.1263 gram $BaSO_4$.

	Calculated for $\left(C_6H_4\left\{\begin{matrix}SO_2NH_2\\CO_2\end{matrix}\right.\right)_2Ba+4H_2O$.		Found.
$(C_7H_6SO_4N)_2$	400	65.69	...
Ba	137	22.49	22.24
$4H_2O$	72	11.82	11.47

From this experiment the conclusion may be drawn that the meta-amide conducts itself towards chromic acid in very much the same way as the para-amide.

In general, then, the conduct of meta-toluenesulphamide towards both alkaline and acid oxidizing agents is like that of the para amide, and no resemblance is noticed between its conduct and that of the ortho-amide. Whether the same is true of all meta compounds it is impossible to say, but judging from the fact that all para-compounds conduct themselves in the same way towards oxidizing agents, and that what is true of one ortho-compound is rue of others, the conclusion is probable that with reference to heir conduct under the influence of oxidizing agents, meta-compounds are allied to para- and not to ortho-compounds.

REVIEWS AND REPORTS.

RECENT PROGRESS IN AGRICULTURAL SCIENCE.

[Continued from Vol. **3**, 145.]

ASSIMILATION.—In its strict sense, assimilation in plants means the process of forming new organic matter out of inorganic materials by the aid of the sun's rays, and is peculiar to chlorophyl-bearing plants. It will be convenient, however, to give the term a somewhat more extended meaning, and to apply it not only to this process, but also to those related processes which furnish the materials for true assimilation, and to consider in the same connection the kinds and sources of these materials.

Essential Elements.—The question what elements are necessary for the growth of the higher plants may be considered as practically settled. A few points may, however, be noted in passing. As is well known, the earlier experiments showed potassium to be one of the elements essential to plant growth, and it was natural that the question should arise whether the functions of this element in the plant could not be performed by other of the alkali metals. Experiments with sodium showed that this element was incapable of taking the place of potassium, and Nobbe has shown that lithium acts as a direct poison to plants. The physiological worth of these three elements increases with their atomic weight: may it not be possible that other elements of the same group having a higher atomic weight may have a still higher worth? An answer to this question has been attempted by Loew,[1] in some water-culture experiments on buckwheat with rubidium. Earlier experiments by Birner and Lucanus with rubidium, gave very unfavorable results, but according to Loew, the abnormal appearances in their plants were exactly those observed by Nobbe to result from the absence of chlorine; and as only rubidium nitrate was used, it was thought desirable to make similar experiments with the chloride, as well as to repeat those with the nitrate.

The latter gave an entirely negative result; but the experiments with the chloride, in comparison with potassium chloride, though not fully successful, seem to show that at least a certain amount of growth may be made by the aid of rubidium. Still better results were obtained in a third experiment in which a much smaller amount of rubidium was used, in the form of nitrate, with the addition of ammonium chloride. In both experiments the plants grew well until the time of fruiting, and from then on fell behind the potassium plant. The plant nourished with rubidium chloride formed no seeds, and that fed with the nitrate only one; but whether this was due to abnormal nutrition or to some other cause does not clearly appear. On the whole the results, though not conclusive, seem to indicate the *possibility* that suitable quantities of rubidium in a properly constituted solution may be able to take the place of potassium.

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[1] Landw. Versuchs-Stationen, **21**, 389.

Another old question which has lately received renewed attention, is that of the necessity or utility of silica to the plant. As regards its necessity, the newer experiments have only confirmed the results of the older ones that silica is entirely non-essential. A somewhat striking proof of this has been given by Höhnel.[1] The pericarp of *Lithospermum arvense* is normally very rich in silica, containing from 13 to 16 per cent. of this substance, while its outermost layers contain probably 70 per cent. Höhnel has, however, succeeded in producing, by means of water culture, ripe seeds of this plant containing at most but minute traces of silica.

It appears, however, from recent experiments that silica, though not essential to the plant, is nevertheless serviceable to it. In Höhnel's experiments it was noticed that the plants grown without silica suffered from plant lice, while neighboring plants which received silica were not thus affected.

Some experiments by Wolff show that silica has more important functions than the simple protection of the plant. Experiments on the growth of the oat plant in aqueous solutions,[2] continued through fourteen years, have led him to the conclusion that silica favors the seasonable and uniform ripening of the grain by causing the death of the leaves at the proper time, which is followed by a translocation of the nutritive matters contained in them to the seeds. Thus in an experiment without silica 30 seeds were produced, with a little silica 90, and with much silica 184. Another function of silica was also revealed in some of these same experiments. The experiments were directed towards ascertaining the minimum amount of the several ash ingredients necessary for the production of an average crop.[3] Thus it was found that the amount of potash could be reduced to about 0.8 per cent. of the dry weight of the plant, that of phosphoric acid to about 0.5 per cent., &c., &c. It was found impossible, however, to produce a single plant which contained *all* the ash ingredients in the minimum quantity. The total ash, it was found, must always be considerably in excess of the sum of the minima of each ingredient. Only when some indifferent mineral substance, like silica, was supplied to the plants, could a normal growth be obtained with the minimum amounts of the other ingredients. The *rôle* of silica in this respect can also be assumed by lime or by phosphoric acid; but these substances, especially the latter, are somewhat costly, while silica is present in an assimilable form in all soils in greater or less quantity. It would thus appear that while silica is not essential to the *plant*, it may be of great importance to the *crop* by enabling it to make a satisfactory growth in a soil which, without the silica, would not furnish a sufficient supply of ash ingredients, or by preventing a useless consumption of phosphoric acid or other ash ingredients, and an unnecessary exhaustion of the land.

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[1] Haberlandt's Wiss. prakt. Untersuchungen, **2**, 160.

[2] Jahresber. Agr. Chem. N. F. **3**, 216.

[3] *Ibid.* 18–19, **1**, 250.

Sources of Plant Food.—That the *carbon* of vegetation is chiefly supplied by the carbon dioxide of the atmosphere has become one of the truisms of botany; but the question whether this is the sole source of the carbon of agricultural plants and crops, or whether the numerous carbon compounds existing in most fertile soils contribute to any considerable extent to their nourishment, is one that has given rise to no little discussion. The well-known experiments of De Saussure and others (compare Johnson's "How Crops Feed," pp. 232 *et seq.*) render it extremely probable that the organic matters ("humus") of the soil may be assimilated by plants, as we know that certain nitrogenous organic matters may be.

Some later experiments point in the same direction. Van Tieghem[1] finds that the embryo of *Mirabilis jalappa* will grow when the endosperm is removed and replaced by a paste of albumin and water, or of potato starch and water, containing the necessary inorganic nutrients. By microscopical examination and otherwise, Van Tieghem satisfied himself that these substances were actually assimilated. From the brief account of these experiments accessible to the writer it is impossible to judge of their accuracy or of the weight which is to be given them, and Böhm[2] on repeating them obtained negative results; but Blociszewski[3] has since repeated and extended them with much the same result as Van Tieghem. Embryos of rye and peas, separated from the endosperm or cotyledons, assimilated starch and sugar, and grew, not indeed as well as those of whole seeds, but decidedly better than those which received no artificial food. The starch grains which lay next to the scutellum of the rye or the epidermis of the radicle of the pea were found to have been attacked and almost entirely dissolved. Embryos of rye also grew when nourished with their own finely-ground endosperm, while embryos of the pea grow no better when embedded in pellets of their own ground cotyledons than without this addition. The pea embryos, on the other hand, seemed to be aided in their growth by a dilute solution of asparagin, while this substance appeared to be of no use, or even harmful, to the rye embryos.

It thus appears that plants may assimilate "organic" matter not only when full grown but also in the first stages of their existence.

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[1] Jahresber. Agr. Chem. 16–17, **1**, 259.

[2] Jahresber. Agr. Chem. 18–19, **1**, 247.

[3] Landw. Jahrbücher, **5**, 145.

A few trials have been made by Stutzer[1] to ascertain what classes of organic substances may be assimilated. He experimented chiefly on young plants of *Brassica rapa*, growing them in an artificial soil composed of sand or pumice-stone and calcium oxalate or tartarate, moistened with a solution of the needful inorganic ingredients. The plants were placed under bell-glasses, from which the carbon dioxide of the air was excluded. They grew vigorously and gained as much as 228 per cent. of dry matter, thus showing that these acids served in some way as a source of carbon. It was possible, however, that they were first oxidized in the plant to CO_2 which was then assimilated, and to test this a second series of experiments was made in the same way, except that a dish of concentrated solution of sodium hydrate was placed inside each bell-glass. Under these circumstances the plants cultivated in the calcium oxalate speedily died and showed a loss of 4 to 7 per cent. of their dry weight in ten or twelve days, thus showing that the oxalic acid could not be utilized as such by the plant, but must first be oxidized to CO_2. The calcium oxalate remaining after these experiments contained notable quantities of carbonates. The plants cultivated in the calcium tartarate, however, behaved differently. Here a growth took place, and an increase in the dry weight of 66 and 69 per cent. in 17 days was obtained.

Other plants, cultivated in the same soil but with only the atmospheric CO_2 excluded, gained fully twice as much in the same time. In all cases the roots were found encrusted with calcium carbonate. This formation of calcium carbonate, Stutzer suggests, may be explained as due to a metathetical reaction between the soluble carbonates of the roots and the oxalate or tartarate of the soil. The different behavior of oxalic and tartaric acid in these experiments Stutzer explains by a reference to their chemical constitution. Oxalic acid consists of two carboxyl groups, from which, apparently, the plant is unable to appropriate carbon directly. Tartaric acid, on the other hand, contains two carboxyl and two alcoholic groups, and from the latter, according to Stutzer, the plant can assimilate carbon without the necessity of a previous oxidation to CO_2. When the plants were cultivated in a bell-jar containing sodium hydrate, only half the carbon of the tartaric acid could be utilized, and a large amount of CO_2 was found in the sodium hydrate solution at the close of the experiment. In the case in which the sodium hydrate was omitted, however, the carbon of the carboxyl groups was also available, being first oxidized to CO_2 and exhaled, and then assimilated by the chlorophyl grains. Hence, the growth in the latter case was about twice as great as in the former, corresponding roughly to the greater amount of assimilable carbon at the disposal of the plant. A confirmation of this hypothesis was given by an experiment in which glycerine was the sole source of carbon. A gain of 126 per cent. of dry substance was made in seventeen days.

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[1] Landw. Versuchs-Stationen, **21**, 93.

As numerous difficulties had to be overcome in experiments of this sort on higher plants, the investigation was continued with chlorophyl-free plants, chiefly with *Penicillium glaucum*, in which, if growth took place at all, it must be at the expense of the "organic" carbon. It was found that oxalic and formic acids, that is, acids containing only carboxyl groups, were incapable of nourishing this plant. Acetic acid and acetates produced an abundant growth, as did also succinic acid. Succinate of iron was also found capable of furnishing carbon to plants of *Brassica rapa* in an atmosphere free from CO_2. Ethyl alcohol, glycerin, sugar, malic acid, citric acid, lactic acid and tartaric acid caused an abundant growth of the fungus, as, according to Stutzer's hypothesis, they should do; but butyric acid, valerianic acid, and amyl alcohol formed noteworthy exceptions, neither sustaining *penicillium* themselves nor permitting its growth in solutions to which glycerin or sugar had been added.

Stutzer's experiments have been repeated by Schmöger,[1] who obtained similar results, but does not regard them as conclusive, since, according to his experiments, the method adopted includes a grave source of error. This source of error lies in the fact that both oxalate and tartarate of calcium are very easily decomposed by the action of bacteria or other organisms into calcium carbonate and carbon dioxide, so that the soil in Stutzer's experiments was a continual source of CO_2. Schmöger found that moist mixtures of calcium oxalate or tartarate with solution of plant food and with sand (the latter may be omitted) contained, after being exposed to the air for some twenty days, very considerable quantities of calcium carbonate and an abundance of bacteria resembling *Bacterium termo*. Similar mixtures were placed in two flasks, heated to boiling on the water-bath, and stoppered with cotton heated to 120°. Two other flasks were filled in the same way, but not heated. One of each pair was opened after twenty days. The contents of the boiled flask contained no CO_2, those of the unboiled flask 0.234 gram. After thirty-four days the other boiled flask contained no CO_2, and the other unboiled one 0.2675 gram. Schmöger also determined the amount of CO_2 absorbed by the potash solution in his vegetation experiments, as well as the combined CO_2 remaining in the soil, and found the two to be approximately equal. In experiments with plants grown in sand alone, the amount of CO_2 exhaled was found to be very small. Schmöger, therefore, concludes that the growth obtained by Stutzer and himself in those experiments in which no potash was present was made by means of the CO_2 exhaled by the artificial soil, and that it is very possible that the small growth obtained in the presence of potash was due to small portions of CO_2 which escaped absorption.

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[1] Jour. f. Landw. 28, 179.

At any rate, in the absence of proof that the experiments were really made in an atmosphere free from CO_2, they furnish no evidence of a direct assimilation of organic carbon compounds by the higher plants.

Experiments with such organic matters as are found in the soil have in general given negative results. Detmer[1] claims to have observed microscopically an absorption of some of the oxidation products of humus (crenic or apocrenic acids) by the rootlets of young peas, and thinks it probable that they contributed to the nourishment of the plants.

Böhm[2] has sought to solve the question by investigating whether bean plants, freed from starch by long vegetation in the dark, could produce starch when supplied with carbon only through their roots. Negative results were obtained in all cases. No starch formation could be detected, and plants grown in a garden soil containing humus lived no longer than those grown in pure sand (with addition of inorganic nutrients).

Moll[3] has made similar experiments and obtained the same result. In no case was the least formation of starch observed, but on the contrary, starch disappeared from leaves containing it when they were placed in an atmosphere free from CO_2, although they remained in connection with the plant, which grew in a moist soil, rich in humus, and presumably containing much CO_2. Leaves were also separated from the plants and arranged with the basal end in an atmosphere containing about 5 per cent. of CO_2, while the upper end was in an atmosphere kept free from this gas. In some cases an intermediate portion of the leaf was exposed to the air, and in others not. The leaves having been made starch-free in the first place, not the least formation of starch could be detected in the portion of the leaf deprived of CO_2, although it took place vigorously in the other portion of the leaf. Comparative experiments were also made on the rapidity of starch formation in starch-free leaves. A leaf was divided lengthwise just at one side of the midrib. One portion was freely exposed to the air, while the base of the portion containing the midrib was surrounded with an atmosphere containing 5.5 per cent. of CO_2. It was found that this abundant supply of CO_2 to the lower end of the leaf was unable to accelerate at all the starch formation, but that the latter went on at sensibly the same rate as in the other half of the leaf. It was likewise found that the CO_2 of the soil was equally unable to accelerate the formation of starch in the leaves. It would, therefore, appear that CO_2 cannot be transferred as such in the plant, even through very short distances, and also that the organic matter in the soils used by Moll was not able to contribute appreciably to the nourishment of the plants. Corenwinder,[4] however, has observed that the leaves of a branch of a young chestnut tree, which was enclosed in an atmosphere free from carbonic acid but not severed from the tree, developed normally, from which fact he concludes that they were nourished by carbonic acid dissolved in the sap. Moll's results certainly throw serious doubt on this conclusion, and it is quite as reasonable to suppose that a transfer of plastic materials from the remainder of the tree took place.

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[1] Jahresber. Agr. Chem. 13-15, **2**, 166.

[2] *Ibid.* 18-19, **1**, 247.

[3] Landw. Jahrbücher, **6**, 327.

[4] Jahresber. Agr. Chem. 18-19, **1**, 299.

The experiments of Böhm and Moll, as well as the very similar ones of Cailletet,[1] while they do not conclusively show that plants may not assimilate carbon from organic compounds, do show that under ordinary circumstances and in ordinary soils the amount of carbon which plants obtain through their roots is at least too small to be of any practical significance. The undoubted value of the humus of the soil and of manures lies partly in the inorganic matters which it contains, but to a far larger degree in the solvent action of the carbonic acid generated by its decay, and in its influence on the physical properties of the soil.

H. P. ARMSBY.

(*To be continued.*)

A TREATISE ON CHEMISTRY. Vol. III. THE CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES ; or, ORGANIC CHEMISTRY. Part I. By H. E. ROSCOE and C. SCHORLEMMER. New York : D. Appleton & Co. $5.00.

The volume of Roscoe and Schorlemmer forms the first part of the third volume of the excellent "Treatise on Chemistry," and in it the consideration of organic chemistry is begun. The authors give a new name to the subject. That in common use is "The Chemistry of Carbon Compounds," but this they claim, and justly, is too broad, as it applies to all the simple compounds of carbon, such as carbonic acid and the whole list of carbonates, which enter so largely into the composition of the inorganic portions of the earth. They adopt the name "Chemistry of the Hydrocarbons and their Derivatives," and it is hard to see what rational objection can be made to this. It certainly describes accurately what it is intended to describe, and this is more than can be said of any of the names now in use. It may be firmly stated that this book is the most readable one on the subject that has appeared in any language ; and this is a very great merit. Hardly a single one of its many predecessors can be *read.* One may serve admirably as a book of reference for the investigator, another as a laboratory guide, and a third as an aid in connection with lectures ; but they cannot be read continuously with much advantage to the reader. The authors have dealt with their subject in a broad way. They have, of course, first had in mind the pure science, and they have endeavored to point out the methods of the science, as well as to give the results of the application of these methods. Admirable descriptions of the facts of the subject are given, with sufficient fulness for the purposes of most students; and references to the sources of information, the original articles in the chemical journals, are found in connection with every important point. Further, the industrial applications of the science receive full attention, not in an off-hand way as is usual, but in such a way as to bring out their full importance. The chapters on petroleum, alcohol, ether, vinegar and soap should be specially mentioned in this connection. The subject of alcohol regarded in its industrial aspects occupies about forty pages of very interesting reading matter. Then, too, the historical side of the science is treated with great clearness and in an interesting way. There is first an introductory chapter which treats of the development of the subject as a whole, and then, as each new group is brought forward, the special history of this group is given. Thus far only one main group of compounds has been considered, viz. the paraffins, or the marsh gas series of hydrocarbons and their derivatives. If the other groups are treated as fully as this one, and considering their importance it is probable that they will be, the completed treatise will be by far the most extensive one in the English language. As regards the way in which the theories are presented, it is plain that the authors have tried to be consistent, and they have succeeded in this better than most other writers; but exception may be taken to some points. It is quite impossible here to discuss the matter in detail, and a few examples must suffice for illustration. The "law of the linking of atoms" is fundamental, and was, of course, discovered through a study of facts established in connection with a very large number of carbon compounds. A proper study of these facts will show clearly that the law is a just induction. The connection between the facts and the law is, however, not made clear by the paragraph on pages 112 and 113. The following sentence occurs on page 129: "This is caused by the rupture of one of the links of a double-linked carbon atom." The language is highly figurative, and though there are certain phenomena known which correspond to this language in some way, the character of these phenomena is too little understood to warrant the use of such expressions as "rupture of links." Surgical chemistry is a subject for which we are not quite prepared. The language is not original with the authors; it is the every-day language of chemistry, and when used cautiously is not dangerous; but it is not right to introduce it in the early part of a text-book, before the exact nature of the facts to which it refers has been explained. But the book is not one to put the reader in a fault-finding mood. The character of Part I. is such that we await with feelings of pleasurable expectancy the appearance of the concluding parts of the volume.

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[1] Jahresber. Agr. Chem. 13-15, 2, 166.

I. R.

ADOLPH STRECKER'S SHORT TEXT-BOOK OF ORGANIC CHEMISTRY. By DR. JOHANNES WISLICENUS. Translated and edited, with extensive additions, by W. H. HODGKINSON and A. J. GREENAWAY. New York: D. Appleton & Co. $5.00.

In the original this book appeared as a new edition of Strecker's "Organic Chemistry." Professor Wislicenus is one of the active chemists of the present time, and has added materially to our knowledge of carbon compounds. He belongs to the advanced wing of German chemical science. He is so thoroughly imbued with the ideas of "bonds," "structure," "valency," and the other outgrowths of modern organic chemistry, that he does not sufficiently recognize the importance of explaining these ideas and showing on what foundation they rest. In his preface, to be sure, he appears cautious. Thus this passage will be found: "In the present state of our science we cannot neglect the frequent use of structural formulæ based on the valency of the chemical elements. Their partial uncertainty and in many points tangible shortcomings need not prevent their use to some extent in a text-book, although their use requires care." This is excellent; but the author's caution forsook him as soon as he began his work, and we find at the very beginning a large number of entirely unexplained structural formulas, the sudden appearance of which is well calculated to dishearten even a brave, earnest student, while the only effect they can have on ordinary minds is hopeless mystification. Let us not be misunderstood. We do not object to the formulas as such. They are in most cases excellent tentative expressions of facts. They do not imply atom-juggling, as some suppose. They are really of very great value; but they are too strong food for infant chemists. To digest them fully, one must have had a preliminary training; severe indigestion will certainly follow the attempt to swallow them whole without this training.

It is scarcely necessary to refer to special cases to prove the correctness of the assertion that the author of this book presents the formulas prematurely. The entire book furnishes the proof. Some glaring cases may be found on page 58, where formulas are given for many cyanogen derivatives in regard to which our knowledge is very limited; on page 62, where certain complex compounds of hydrocyanic acid with metallic chlorides are dissected in such a way as to suggest a mass of knowledge which we do not possess; on page 94, which presents formulas for compounds of urea and oxide of mercury, etc. If the author had intended simply to inform his readers in regard to the latest views actually held concerning the structure of organic compounds, without showing exactly what the formulas mean, his book would necessarily be regarded as a success, but this was not his intention. The work was written for beginners, and for them, we submit, it is not suited. On the other hand, it must be acknowledged that it contains a large mass of valuable information systematically arranged and accurately stated, and if used in connection with other books, as for example with that of Roscoe and Schorlemmer, or in connection with a good course of lectures, it will serve a good purpose. The translation is fair, though the translators are constantly under the influence of the German idiom. Stilted sentences are met with throughout the book. This, however, is almost inevitable, and we are not disposed to find fault, for, though the language is clumsy, the meaning is not obscured to any great extent. I. R.

NOTES.

On a new Gas Regulator.

In the description of a new gas regulator by Mr. Wilson in Vol. 3, No. 5, of this Journal, I note in the form of the apparatus a considerable advantage over that with which I had been familiar. If we combine this with that of Mr. Kemp, described in the Handbook of Chemical Manipulations by G. Williams, page 49, we shall have the desired apparatus, further simplified, while retaining all of the advantages of each. Such an arrangement may be represented by Figure 1, if we conceive the arm ED to be shortened, so as to

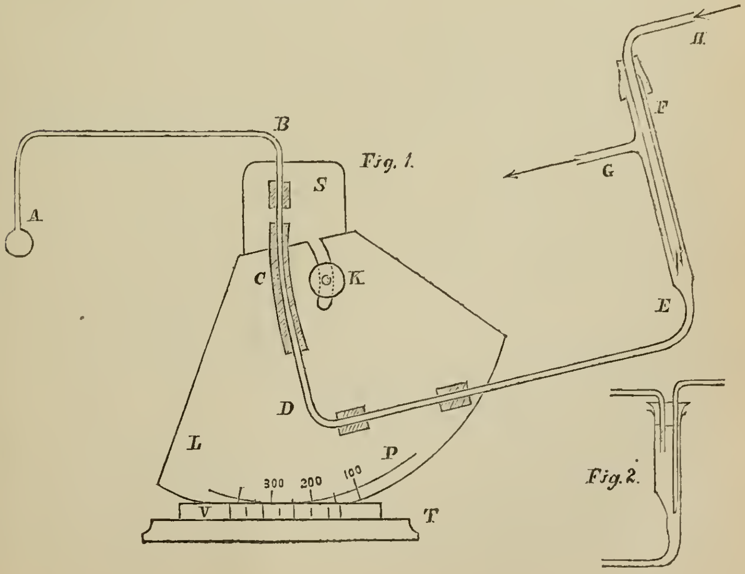

Fig. 1.

Fig. 2.

make CDEF form a simple U tube, and held rigid in a vertical position, and the tube H to slide up and down within the limb F, determining by its position the temperature to which the bulb A may be heated.

Having made an instrument of this kind, I found some difficulties in its working, which are avoided in the following simpler apparatus. This instrument, although rather bulky, may be quickly made, and not only enables one to keep an air, oil or water-bath at, approximately, a constant temperature, but also by a simple adjustment, to nearly eliminate variations due to the barometric pressure and the temperature of the laboratory, and to then adjust it for any desired temperature.

Its construction may be understood by reference to Figure 1, drawn about one-sixth of its size. A thermometer tube, bent at B, is supported by the stand ST. The thin board LK is fastened to the upright S by a screw at C, so that it may be revolved about C and be clamped in any desired position by the thumb-screw K.

The tube F, with inner diameter about 3 mm., is joined to a rather stout tube with small bore, and the latter is bent at E and D. The tube H is slid within the tube F, and is held firm by the rubber tube, which grasps them both and is tied. The tube ED is nearly filled with *clean* mercury, then joined to B by the heavy rubber tube C, about 70 mm. in length, leaving sufficient room between the tubes to allow of some motion, and then fastened to the board LK. A scale of equal subdivisions is attached to the strip of wood V, which is fastened to T. The lower end of H is made with a narrow slit in it, at least 5 mm. long, which is readily done by first piercing a hole and then drawing it out at that point.

The arm HE is brought to its lowest position, and by blowing into G, all excess of mercury is driven out through H. The arm is then raised until the lower end of the tube H just touches the surface of the mercury. A single mark made on the line P will be opposite to some division of the scale V, which latter will then serve as the index by which the several divisions of the scale P may be made by trials. If the barometric pressure decreases or the temperature of the atmosphere increases, this index point will be found further to the right, but may be employed with the scale previously made on P, with an error of less than 4 or 5 degrees. It will thus be seen that by raising the arm HE and fixing it in any position, gas can pass until the expansion of the air in the bulb A increases the pressure enough to force the mercury up into the tube F and diminish the passage of gas.

As the flame which is governed by this regulator may be extinguished, it is best to have a minute gas-jet constantly burning, and so placed that it will light the gas when it escapes again.

It is preferable to fuse the tube H to the top of F, and so avoid the rubber joint; on the other hand, the side joint G may be substituted by the arrangement indicated in Figure 2.

F. P. Dunnington.

University of Va., *April*, 1882.

Artificial Quinine. (?)

"The discovery of H_2N has just furnished me with the means of realizing a synthesis desired by all chemists, and the object of a reward offered by the Society; this synthesis is that of quinine. I would at once communicate to the Academy the details of the very simple operation in which H_2N furnishes very pure sulphate of quinine, if it were not proper that I should first submit to medical proofs this sulphate, all the properties of which are identical with those of the sulphate prepared from quinquinia.

"The Academy, in accepting the deposit of the sealed packet accompanying this letter, will give me the opportunity to devote the necessary time to therapeutic studies. I will be grateful to them for it. E. J. MAUMENÉ."

The above note is taken literally from a recent number of the *Comptes rendus.* The remark "important if true" seems called for. Why, if this synthesis has actually been accomplished, the chemical world should be kept in suspense in regard to it, it is difficult to say. As we see it, there is something puerile about this mysterious sealed-packet method of announcing discoveries. If the depositor is not quite sure of his discovery, let him be silent; but if he is sure of it, in the name of all that is outspoken and truth loving, let him boldly proclaim it. The method seems specially adapted to the encouragement of abortions, which Heaven knows! are common enough without the necessity of being made respectable by a great Academy. I. R.

Processes for Direct Coppering of Castings of Iron and Steel.

F. WEIL gives an account of the processes devised by him for the direct coppering of castings of iron and steel without the use of any intermediate coating of plumbago or other material upon the surface of the casting.

The deposit of copper by this method is so homogeneous and so faithfully reproduces the most delicate details of ornamentation as to give to articles so coppered the artistic value of bronze, and at the same time is so firmly adherent that castings coppered by this process have remained exposed to the weather for ten years without requiring any retouching.

The alkaline organic baths used in the process present several advantages over the ordinary alkaline baths used in electroplating. The cyanides, which are both injurious to the health of the workmen and expensive, are replaced by organic acids or by glycerin, both of which are cheap and have the advantage of not being decomposed in the operation. Thus the baths require no renewal of organic material, and act continuously provided the necessary amount of oxide of copper is added from time to time. Finally, the well-known property of alkaline organic solutions of dissolving oxide of iron easily and rapidly without attacking the metal itself, always renders the cleansing of the castings perfect, as the bath finishes the cleansing of articles before coppering them.

The process is carried on in three different ways according to local conditions and the different applications of the articles to be coppered.

The first method consists in plunging the articles in the bath in contact with strips of zinc. The coppering begins immediately, and, according to the alkalinity of the bath and the destination of the articles to be coppered, requires a variable time from a few minutes to several hours.

The second process, which has been employed with great success for coppering the street lamps of a large city, consists in placing in the vessel containing the bath and the objects to be plated porous jars filled with a strong solution of caustic soda, in which are placed plates of zinc connected with the articles in the bath by a coarse copper wire. The time required for depositing a moderately thick coating of copper, such as required by candelabra, etc., is very short.

The third process consists in the use of the same baths as in the first and second processes, in conjunction with a dynamo-electric machine.

The baths, as has been said, only require the addition of a certain amount of oxide of copper from time to time, and by a simple method of titration, also devised by M. Weil, the exact amount of copper oxide to be added can be readily and quickly determined.

These processes can also be applied to the deposition of all metals, such as nickel, cobalt, antimony, tin, etc., upon castings of iron and other metals.—(*Comptes rendus*, 93, 1018.)

R. D. C.

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SCHMIDT, F. Ueber Fettbestimmungen in der Milch mittelst des Lactobutyrometers.

TUBBE, C. Ueber die Einwirkung von Iodacthyl auf Anhydroacetdiamidotoluol.

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F. W. C.

Vol. IV. [July, 1882.] No. 3.

AMERICAN CHEMICAL JOURNAL.

ON THE SULPHO-CINNAMIC ACIDS.

By Chase Palmer,
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As is well known, when chlorine, nitric acid, sulphuric acid, etc., act upon aromatic hydrocarbons containing such groups as CH_3,C_2H_5, etc., the principal product is usually a para-compound, while the isomeric ortho-compound is formed at the same time in smaller quantity. If, on the other hand, the carboxyl group is present in the hydrocarbon, the principal product is usually a meta-compound. If a neutral group be interposed between the benzene nucleus and the acid residue, as in the compound $C_6H_5.CH_2.COOH$, the carboxyl group loses the power of determining the position of substituting groups subsequently entering the nucleus. Beilstein and Kuhlberg[1] have shown that phenylacetic acid, $C_6H_5.CH_2.COOH$, conducts itself in the same way towards nitric acid as toluene, for, by nitrating phenylacetic acid, para- and ortho-nitrophenylacetic acids are formed; para- and ortho-nitrophenylpropionic acids are likewise obtained by the action of nitric acid on phenylpropionic acid. These investigations further show that from nitric acid and cinnamic acid, $C_6H_5.CH{=}CH.COOH$, para- and ortho-nitrocinnamic acids are formed.

Rudnew has observed[2] that two sulphocinnamic acids are formed when cinnamic acid is dissolved at the ordinary temperature in fuming sulphuric acid. The principal product is parasulphocinnamic acid; while the second one, which is formed in very small quantity, is believed by Rudnew to be the meta and not the ortho compound, the formation of which would naturally be expected. This metasulphocinnamic acid was converted, by fusion with potassium hydroxide, into oxybenzoic acid. Rudnew attempted to oxidize it with sulphuric acid and potassium bichromate, but failed to obtain a satisfactory result.

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[1] Annalen der Chemie, **163**, 140.

[2] Annalen der Chemie, **173**, 8.

The conduct of the substance towards the chromic acid mixture led to the suspicion that though described by Rudnew as a meta compound, it might possibly prove to be an ortho compound. It seemed probable that, if the two sulphuric acids were converted into the corresponding amides, and then oxidized, it would be an easy matter to recognize even a small quantity of the ortho derivatives, if present. This should be the substance which was discovered and described by Remsen and Fahlberg[1] under the name benzoic sulphinide, $C_6H_4\left\{\begin{matrix}CO\\SO_2\end{matrix}\right\}NH$. It has a very marked sweet taste, and its presence can easily be detected by means of this property. As will be seen, the results reached are not quite satisfactory, though they are rather confirmatory of Rudnew's view than otherwise. In connection with the main work some new derivatives of parasulphaminecinnamic acid have been studied.

Sulpho-Cinnamic Acids.

One sulphocinnamic acid has been known for several years. Marchand obtained it first by treating cinnamic acid with sulphuric acid, and described the barium and lead salts.[2] Herzog subsequently prepared it in a purer condition and added a few salts to Marchand's lists.[3] Rudnew's method for the preparation of the sulphocinnamic acids involves the use of a much smaller quantity of fuming sulphuric acid than had been previously employed. The sulphuric acid which he used contained 20 per cent. of sulphuric anhydride. He also found that the yield of the sulphocinnamic acids is much larger if cinnamic acid be treated with fuming sulphuric acid of this strength, than when a weaker sulphuric acid is employed. The formation of a resinous product is thereby almost entirely avoided, while such a product always attends the use of a sulphuric acid containing a smaller proportion of anhydride, thus causing considerable loss of material.

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[1] This Journal, **1**, 170.

[2] Journal prak. Chemie, **16**, 60.

[3] *Ibid.* **29**, 51.

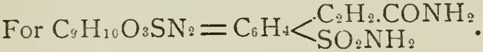
The separation of the two sulphocinnamic acids is most easily accomplished by means of their acid barium salts. The acid barium salt of parasulphocinnamic acid crystallizes in long needles which are very difficultly soluble in cold water. The corresponding salt of the isomeric acid is more easily soluble than the para salt. This method Rudnew recommends, and I have adopted it for the preparation and isolation of the sulphocinnamic acids for my experiments.

60 grams of pure and finely powdered cinnamic acid were gradually dissolved in fuming sulphuric acid containing 20 per cent. anhydride. The mixture was kept cool during the operation. Each portion of the cinnamic acid was completely dissolved before the succeeding portion was added. In the act of solution a slight elevation of temperature was observed. When the cinnamic acid was completely dissolved, the liquid was diluted with five or six times its volume of water. The sulphuric acid was neutralized with barium carbonate until barium chloride caused no further precipitate. After the removal of the precipitated barium sulphate, the solution, containing the free sulphonic acids, was divided into two equal portions. One-half was exactly neutralized with a solution of barium hydroxide; the other portion was then added to it. Upon evaporating the solution to a sufficient concentration, the acid para barium salt crystallized out in long needles. A small quantity of the para salt was obtained by further evaporation.

The mother liquor was then evaporated to a small volume, when the meta acid barium salt made its appearance in concretionary aggregates. To remove from the meta salt the para salt, which still adhered to it, it was repeatedly boiled with a small quantity of water, and was thus obtained quite pure. A slight color was removed with animal charcoal.

Parasulphocinnamide.—The barium was exactly precipitated from a hot aqueous solution of the acid para barium sulphocinnamate by means of a solution of potassium carbonate. After the precipitate of barium carbonate was removed, the aqueous solution of the potassium salt was evaporated to dryness. From the dry neutral potassium salt the double amide is obtained by gently heating the salt with phosphorus pentachloride. The acid chloride is a semi-liquid which solidifies on cooling. The chloride by treatment with concentrated aqueous ammonia is converted into the amide. The para double amide is obtained in a pure condition by three or four recrystallizations from hot water. It crystallizes in clusters of needles, which are easily soluble in hot water, but more difficultly soluble in cold water. It fuses at 218° C. (uncorrected). The air-dried amide was analyzed with the following result:

0.1265 gram substance gave 13.9 cc. N at 756 mm. pressure, and 21.5° C. = 0.0156904 gram N.



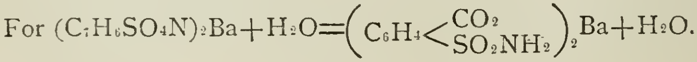
For $C_9H_{10}O_3SN_2 = C_6H_4 < \begin{array}{l} C_2H_2.CONH_2 \\ SO_2NH_2 \end{array}$.

	Calculated.		Found.
$C_9H_{10}O_3S$	198	87.61	...
N_2	28	12.39	12.40
	226	100.00	

Oxidation of the para amide.—A small quantity of the pure amide was placed in a flask and treated with the usual oxidizing mixture of sulphuric acid, potassium bichromate and water. The mixture was heated over a small flame, when a violent reaction occurred, and in a few minutes the amide was completely oxidized. Upon diluting the solution with water the product of oxidation crystallized out, and after the solution had become cold it was placed on a filter and thoroughly washed. The product was redissolved in hot water and purified by recrystallization. It is an acid, and crystallizes in flat prisms; it is decomposed at a temperature of about 280° C. without melting. It is very difficultly soluble in cold water, but more easily in hot water. Its properties correspond to the properties which Remsen ascribes to para-sulphamine-benzoic acid, obtained by the oxidation of paratoluene-sulphamide with the chromic acid mixture.

The *barium salt* is very soluble in water, and crystallizes in granular aggregates from the concentrated aqueous solution. An analysis of the air-dried salt was made.

0.2987 gram Ba salt lost 0.0097 gram H_2O at 120° C., and gave 0.1234 gram $BaSO_4$ = 0.07255 gram Ba.



For $(C_7H_6SO_4N)_2Ba + H_2O = \left(C_6H_4 < \begin{array}{l} CO_2 \\ SO_2NH_2 \end{array} \right)_2 Ba + H_2O$.

	Calculated.		Found.
$C_{14}H_{12}S_2O_8N_2$	400	72.08	...
Ba	137	24.68	24.29
H_2O	18	3.24	3.24
	555	100.00	

Parasulphamine-Cinnamic Acid.

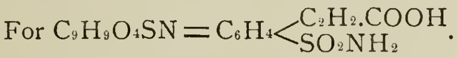
The double amide already described was heated on a water bath with a solution of sodium hydroxide. When the ammonia ceased to be evolved, the solution was neutralized with hydrochloric acid, and filtered to remove any undecomposed amide.

On acidifying the solution with hydrochloric acid a crystalline precipitate was formed, which, redissolved in boiling water, crystallized, as the solution cooled, in long needles. Only one crystallization from hot water was necessary to purify the product.

When dry, it was analyzed.

I. 0.1953 gram substance gave 10.3 cc. N at 753 mm. pressure, and 17° C. = 0.01183385 gram N.

II. 0.1979 gram substance gave 10.8 cc. N at 756.5 mm. pressure, and 18.8° C = 0.01230653 gram N.



For $C_9H_9O_4SN = C_6H_4{<}\begin{matrix} C_2H_2.COOH \\ SO_2NH_2 \end{matrix}$.

	Calculated.		Found. I.	Found. II.
$C_9H_9O_4S$	213	93.83	...	...
N	14	6.17	6.06	6.22
	227	100.00		

The substance possesses the properties of an acid. At 21° C. 0.058 parts are soluble in 100 parts of water. It is difficultly soluble even in hot water. From a hot aqueous solution it crystallizes in long thick needles. Alcohol dissolves it quite readily, and ether with difficulty. At 250° C. it decomposes without melting.

Barium salt.—This salt is obtained by boiling parasulphamine-cinnamic acid with an excess of barium carbonate. From the filtered solution the salt crystallizes in thick needles. It is soluble in cold water, and very easily soluble in hot water.

The air-dried salt was analyzed.

I. 0.26 gram Ba salt lost 0.0149 gram H_2O at 120° C., and gave 0.0966 gram $BaSO_4 = 0.05679$ gram Ba.

II. 0.235 gram Ba salt lost 0.0135 gram H_2O at 120° C., and gave 0.0875 gram $BaSO_4 = 0.05144$ gram Ba.

For $(C_9H_8SO_4N)_2\ Ba + 2H_2O$.

	Calculated.		Found. I.	Found. II.
$(C_9H_8SO_4N)_2$	452	72.32	...	...
Ba	137	21.92	21.84	21.88
$2H_2O$	36	5.76	5.73	5.74

Calcium salt.—The calcium salt is obtained by treating a boiling solution of parasulphamine-cinnamic acid with finely powdered Iceland spar. The salt crystallizes in clusters of fine needles, which are not very difficultly soluble in water.

Analyses of the air-dried salt were made.

I. 0.3934 gram Ca salt lost 0.0141 gram H_2O at 120° C., and gave 0.1053 gram $CaSO_4 = 0.03097$ gram Ca.

II. 0.3864 gram Ca salt lost 0.0139 gram H_2O at 120° C., and gave 0.1033 gram $CaSO_4 = 0.03038$ gram Ca.

For $(C_9H_8SO_4N)_2Ca + H_2O$.

	Calculated.		Found. I.	Found. II.
$(C_9H_8SO_4N)_2$	452	88.64	...	...
Ca	40	7.84	7.87	7.86
H_2O	18	3.52	3.58	3.59
	510	100.00		

Oxidation of Parasulphamine-Cinnamic Acid.

It has already been stated that by heating the para double amide with a solution of caustic soda, ammonia is evolved and an acid containing but one nitrogen atom is formed.

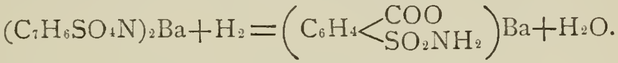
9 grams of this acid were placed in a balloon flask with 20 grams of potassium bichromate and 30 grams of concentrated sulphuric acid, diluted with three times its volume of water. The mixture was heated for four or five hours. At the end of this time it was diluted with water, and, after it had cooled, the insoluble product which had crystallized out was placed on a filter

and thoroughly washed. It was redissolved in hot water, from which it crystallized out in flat plates as the solution cooled. After two or three crystallizations the product was obtained colorless and perfectly pure.

It is very difficultly soluble even in hot water, and is decomposed at 280° C. without fusing. The barium salt is very soluble in water, but crystallizes from a concentrated solution. The salt, dried in the air at the ordinary temperature, was analyzed with the following result:

I. 0.3385 gram Ba salt lost 0.0107 gram H_2O at 120° C., and gave 0.1426 gram $BaSO_4 = 0.0838$ gram Ba.

II. 0.2864 gram Ba salt lost 0.0088 gram H_2O at 120° C., and gave 0.1221 gram $BaSO_4 = 0.0717$ gram Ba.

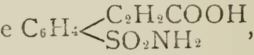


For $(C_7H_6SO_4N)_2Ba+H_2=\left(C_6H_4<\begin{matrix}COO\\SO_2NH_2\end{matrix}\right)Ba+H_2O$.

	Calculated.		Found.	
			I.	II.
$(C_7H_6SO_4N)_2$	400	72.08	...	...
Ba	137	24.68	24.75	25.03
H_2O	18	3.24	3.16	3.07
	555	100.00		

The acid just described is identical with the acid obtained by oxidizing the para double amide of cinnamic acid, and possesses all the properties of para-sulphamine-benzoic acid, obtained by oxidizing paratoluene-sulphamide with the chromic acid mixture.[1]

The acid formed by the action of caustic soda on the para double amide of cinnamic acid is therefore $C_6H_4<\begin{matrix}C_2H_2COOH\\SO_2NH_2\end{matrix}$, as we would expect, and the name para-sulphamine-cinnamic acid describes its constitution.



Metasulpho-Cinnamic Acid.

When the para acid barium salt had been entirely removed from the meta acid barium sulphonate, the aqueous solution of the latter was treated with a solution of potassium carbonate in sufficient quantity to exactly precipitate the barium. The solution was filtered from the precipitated barium carbonate and evaporated to dryness. The perfectly dry meta potassium salt (five parts) was treated with phosphorus pentachloride (seven parts), the mixture being kept cool during the operation. When the action of the pentachloride upon the salt had ended, concentrated aqueous ammonia was added in excess. On standing several hours the amide crystallized out. It is more easily soluble in cold water than the corresponding para amide. As the quantity of the meta amide in my possession was small, it was very difficult to obtain it perfectly pure.

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[1] Annalen der Chemie, 178, 297 ff.

Oxidation of the meta amide.—Since Rudnew was unable to obtain a satisfactory result by oxidizing meta-sulpho-cinnamic acid with the chromic acid mixture, I subjected the double amide to the oxidizing action of potassium permanganate, hoping thereby to obtain an easily recognizable product.

The following proportions were taken: 5 grams of the amide, 20 grams of potassium permanganate, and 200 cc. water, made distinctly alkaline with a small quantity of caustic soda solution.

The mixture was heated for eight hours on a water-bath; reduction of the permanganate occurred with evolution of ammonia. When the ammonia had ceased to be evolved, the reduction of the permanganate was completed by means of sulphurous acid, and the solution, filtered from the manganese oxides, was evaporated to a small volume. It was then acidified, and as no precipitate was formed, the solution was evaporated to dryness, and the dry mass repeatedly treated with alcohol. Upon evaporating the alcoholic solution to dryness, an organic residue was left, which is readily soluble in water. It possesses no distinctly sweet taste, and its other properties differ materially from the properties of benzoic sulphinide, which Remsen and Fahlberg obtained by oxidizing orthotoluene sulphamide in a similar manner. As far as could be judged from the experiments performed, not a trace of benzoic sulphinide was formed in the oxidation of metasulphocinnamide with potassium permanganate. Further, a small quantity of the meta amide was fused with potassium hydroxide, but I was unable to detect the presence of salicylic acid in the product.

If these results, although in themselves of a negative character, be taken in connection with Rudnew's positive results, namely, that by fusion with potassium hydroxide the sulphocinnamic acid yields oxybenzoic acid, the proof is sufficiently strong to justify the conclusion that the sulphocinnamic acid, which is formed in small quantity by the action of sulphuric acid on cinnamic acid, is not orthosulphocinnamic acid. It may, however, be regarded as an open question whether Rudnew's acid was really metasulphocinnamic acid. The conduct of the substance towards chromic acid seems particularly to justify this, as it has been shown[1] that meta compounds conduct themselves like para compounds, easily yielding oxidation products, while this so-called meta acid breaks up when oxidized. The small quantity of the acid formed prevented a more complete study.

The work described in this paper was undertaken at Professor Remsen's suggestion, and was conducted in the chemical laboratory, under his supervision and with his assistance.

April, 1882.

Contributions from the Chemical Laboratory of Harvard College.

XXI.—DIBROMACRYLIC ACID.[2]

By Henry B. Hill.

In a communication upon furfurol and certain of its derivatives which I laid before the American Academy of Arts and Sciences a year ago, I described a dibromacrylic acid[3] which O. R. Jackson and I had some time before obtained from mucobromic acid by the action of alkalies. Although we had not been able to prepare the acid in a state of perfect purity, still our results seemed to us sufficient for its identification; and since it then appeared that a more extended study of it would interfere with other investigators in the same field, further work upon it had been for the time given up. Not long afterward it became evident that our hesitation upon this account had been quite unnecessary; but it was not until recently that I was able to take up again the study of this acid. I have now obtained results which correct our previous observations in several important particulars.

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[1] This Journal, 3, 142.

[2] Proceedings Amer. Academy. Communicated by the Author.

[3] This Journal, 3, 106; and Proceedings Amer. Academy, 16 (N. S. viii), 192.

For the preparation of the acid, O. R. Jackson and I used chiefly the barium salt, which crystallized well from water or dilute alcohol, and which gave us constant analytical results. The air-dried salt lost nothing *in vacuo* over sulphuric acid, or when heated to 80°, and the percentage of barium which it contained agreed closely with that required by the formula $Ba(C_3HBr_2O_2)_2$. We therefore with little hesitation considered the salt anhydrous, and were inclined to ascribe the slight loss of weight which we noticed at 100° to a slow decomposition. The acid made from carefully prepared barium salt crystallized well, melted quite sharply at 83–84°, but on analysis proved to contain too high a percentage of bromine. Since the acid made from the lead salt had given us precisely the same unsatisfactory results, we thought it probable that the impurities which were found in the acid thus made were introduced by a decomposition of the acid itself in its liberation from its salts. A more careful study of this reaction subsequently convinced me, however, that such was not the case. Certainly no carbonic dioxide, bromacetylen, or hydrobromic acid could be detected as resulting from such decomposition when dilute sulphuric acid was added in slight excess to a boiling aqueous solution of the barium salt. I therefore turned my attention to a further purification of the salts.

Since repeated recrystallization of the barium salt failed to give me any much better product, I thought it worth while to determine the variation of composition introduced by one set of crystallizations from water. I therefore dissolved 30 grams of white well crystallized salt (A) in 380 cc. of hot water. On cooling, 6.5 grams of the salt (I) separated, and by successive filtration, evaporation, and cooling, I obtained the fractions (II) 8.9 grams, (III) 6.9 grams, and (IV) 4.8 grams, the remaining 2.9 grams being lost in the filter-papers upon which the successive portions were dried. An analysis of these air-dried salts gave the following results:

A. 0.5669 gram substance gave 0.2239 gram $BaSO_4$.
I. 0.5713 gram substance gave 0.2276 gram $BaSO_4$.
II. 0.5139 gram substance gave 0.2036 gram $BaSO_4$.
III. 0.5665 gram substance gave 0.2231 gram $BaSO_4$.
IV. 0.5003 gram substance gave 0.1941 gram $BaSO_4$.

	Calculated for $Ba(C_3HBr_2O_2)_2$.	Calculated for $Ba(C_3HBr_2O_2)_2.H_2O$.	Found.				
			A.	I.	II.	III.	IV.
Ba	23.03	22.35	23.21	23.43	23.29	23.15	22.80

From these results it was evident that the barium salt contained a persistent impurity which could not be removed by fractional crystallization, and that the constancy of its composition was accidental. I next tried the beautifully crystalline acid potash salt which I have already described,[1] and found that it gave results which were all that could be desired. This salt can easily be made by neutralizing a weighed amount of the ordinary acid melting at 82–84° with potassic carbonate, and adding to the hot solution an equal amount of the acid dissolved in a little hot water. As the solution cools the salt separates in long silky needles, which after a few recrystallizations from hot water yield an acid whose melting point is constant. The loss in recrystallization is comparatively small, since the salt is but sparingly soluble in cold water and dissolves very freely in hot. The analyses which I have made of the acid prepared in this way show its perfect purity.

I. 0.2183 gram substance gave by the method of Carius 0.3573 gram AgBr.

II. 0.2127 gram substance gave 0.3476 gram AgBr.

III. 0.2530 gram substance gave 0.4137 gram AgBr.

Calculated for $C_3H_2Br_2O_2$.		Found.		
		I.	II.	III.
Br	69.56	69.66	69.56	69.60

The pure acid melts at 85.5–86°, but in other respects does not differ essentially in its physical properties from the product which I have already described. The solubility of the acid was determined by neutralizing with baric carbonate an aqueous solution of the acid prepared according to the method of V. Meyer, and precipitating with sulphuric acid the barium dissolved.

I. 12.7854 grams of a solution saturated at 17.5° gave 0.3107 gram $BaSO_4$.

II. 13.5723 grams of a solution saturated at 17.5° gave 0.3303 gram $BaSO_4$.

III. 10.8488 grams of a solution saturated at 18° gave 0.2695 gram $BaSO_4$.

IV. 9.7341 grams of a solution saturated at 18° gave 0.2434 gram $BaSO_4$.

According to these determinations, the aqueous solution saturated at 17.5° and 18° contains the following percentages:

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[1] *Loc. cit.* p. 194.

	17.5°.		18°.	
I.		II.	III.	IV.
4.80		4.81	4.90	4.94

Baric Dibromacrylate, $Ba(C_3HBr_2O_2)_2.H_2O$.—The barium salt prepared by neutralizing a solution of the pure acid with baric carbonate did not differ in outward appearance from the salt made directly from mucobromic acid by the action of baric hydrate, but proved on analysis to contain a percentage of barium materially lower than that which O. R. Jackson and I had previously obtained, and closely agreeing with that required by one molecule of water of crystallization. When dried by exposure to the air the salt lost nothing over sulphuric acid or when heated to 85°, but by long continued heat at 100° (75 to 100 hours), or more rapidly at 120°, it gave up its crystal water without showing any signs of decomposition.

I. 0.6642 gram of the air-dried salt gave by precipitation 0.2540 gram $BaSO_4$.

II. 0.6392 gram of the air-dried salt gave on ignition with H_2SO_4 0.2434 gram $BaSO_4$.

III. 0.5300 gram of the air-dried salt lost at 120° 0.0161 gram H_2O.

IV. 1.9253 gram of the air-dried salt lost at 100° 0.0548 gram H_2O.

V. 1.1582 gram of the air-dried salt lost at 100° 0.0351 gram H_2O, and gave by precipitation with H_2SO_4 0.4408 gram $BaSO_4$.

Calculated for $Ba(C_3HBr_2O_2)_2.H_2O$.		Found.				
		I.	II.	III.	IV.	V.
Ba	22.35	22.48	22.39	...	...	22.28
H_2O	2.94	...	...	3.04	2.85	3.03

The solubility of the salt was also determined.

I. 9.4276 grams of an aqueous solution saturated at 18° gave by precipitation 0.2214 gram $BaSO_4$.

II. 8.4088 grams of a solution saturated at 18° gave 0.1917 gram $BaSO_4$.

According to these determinations the aqueous solution of the salt saturated at 18° contains the following percentages of the anhydrous salt:

I.	II.
6.00	5.82

Plumbic Dibromacrylate, $Pb(C_3HBr_2O_2)_2.H_2O$.—The lead salt which, according to the analyses made of former preparations, was anhydrous when made from the pure acid by neutralization with plumbic carbonate, or from the acid potassium salt by precipitation with plumbic acetate, likewise proved to contain one molecule of water of crystallization.

I. 0.5972 gram of the air-dried salt lost at 100° 0.0161 gram H_2O, and gave by ignition with H_2SO_4 0.2655 gram $PbSO_4$.

II. 1.0438 gram substance dried over H_2SO_4 lost at 100° 0.0283 gram H_2O, and gave by ignition with H_2SO_4 0.4622 gram $PbSO_4$.

	Calculated for $Pb(C_3HBr_2O_2)_2.H_2O$.	Found.	
		I.	II.
Pb	30.31	30.37	30.25
H_2O	2.64	2.70	2.71

Calcic Dibromacrylate, $Ca(C_3HBr_2O_2)_2.3H_2O$.—The calcium salt made from the pure acid crystallized in long clustered needles, which gave on analysis results identical with those which O. R. Jackson and I formerly obtained.

I. 2.1502 grams of the air-dried salt lost at 80–85° 0.2034 gram H_2O.

II. 1.2264 gram of the air-dried salt lost at 95–100° 0.1171 gram H_2O.

III. 1.8124 gram of the air-dried salt lost at 100° 0.1755 gram H_2O.

	Calculated for $Ca(C_3HBr_2O_2).3H_2O$.	Found.		
		I.	II.	III.
H_2O	9.78	9.46	9.55	9.68

I. 0.4393 gram of the salt dried at 100° gave on ignition with H_2SO_4 0.1199 gram $CaSO_4$.

II. 0.6161 gram of the salt dried at 100° gave on ignition with H_2SO_4 0.1674 gram $CaSO_4$.

	Calculated for $Ca(C_3HBr_2O_2)_2$.	Found.	
		I.	II.
Ca	8.03	8.03	7.99

Potassic Dibromacrylate, $KC_3HBr_2O_2$.—The analysis of the potassium salt made by neutralizing the pure acid with potassic carbonate showed that it was anhydrous, as it had previously been described.

I. 0.7334 gram of the salt dried over H_2SO_4 gave on ignition with H_2SO_4 0.2373 gram K_2SO_4.

II. 0.7507 gram of the salt dried over H_2SO_4 gave 0.2427 gram K_2SO_4.

	Calculated for $KC_3HBr_2O_2$.	Found. I.	Found. II.
K	14.58	14.53	14.51

Although many unsuccessful attempts had previously been made to prepare brompropiolic acid in a pure state, it seemed to me not impossible that the prolonged action of alkalies in the cold might remove from the dibromacrylic acid a molecule of hydrobromic acid, and that a purer product might thus be obtained. I found, however, that the reaction was extremely slow, at least with baric hydrate. An aqueous solution which contained one molecule of baric hydrate to each molecule of dibromacrylic acid was strongly alkaline even after standing for fifteen days, and gave on acidification and extraction with ether the compound of brompropiolic and dibromacrylic acids which has already been described. After recrystallization from ligroin the substance melted at 103°, and gave on analysis the following result:

0.2535 gram substance gave 0.3766 gram AgBr.

	Calculated for $C_6H_3Br_3O_4$.	Found.
Br	63.33	63.22

Since I had before noticed that this intermediate product could be obtained from dibromacrylic acid by the action of baric hydrate in the course of a few hours, and that malonic acid was formed even in the cold after the lapse of several months, it was evident that further attempts in this direction were useless.

XXII.—ON THE CRYSTALLINE FORM OF α-DICHLORACRYLIC ACID.

By W. H. Melville.

(Communicated by H. B. Hill.)

Although the physical properties of the β-dichloracrylic acid of Wallach[1] are decidedly different from those which W. Z. Bennett and I found to be characteristic of the dichloracrylic acid made from mucochloric acid,[1] a difference which appeared to be fully confirmed by a comparison of the salts of the two acids, still it seemed to me desirable to prove with a little more precision the difference between the two. Since Wallach had made no determinations of the solubility of his acid or its salts, and moreover thought[2] that little weight should be attached to the determinations of crystal-water which he had as yet published, there remained no definite, well-established points of difference except the melting points (86° and 77°) and a difference in the crystalline form of the potassium salt: one crystallizing in needles, the other in hexagonal plates. Since the β acid had been obtained in measurable crystals and fully described in Wallach's first paper, although we had previously been unable to get measurable crystals of our acid, I made fresh attempts with larger quantities of material than had then been at our disposal. I found that by the slow cooling of a warm, moderately dilute solution in chloroform, well-developed crystals could be obtained, although the determination of the crystals was rendered difficult on account of the rapid roughening of their faces when exposed to the air. Dr. W. H. Melville succeeded, however, in making the necessary measurements, and to his kindness I am indebted for the following description. The purity of the material used was determined by analysis.

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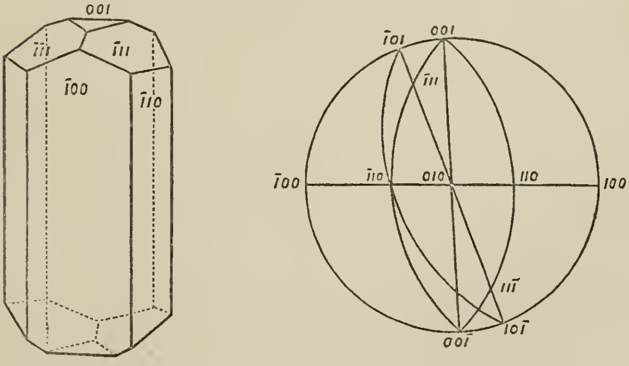
[1] Annalen der Chemie, 93, 19.

0.2061 gram of the substance gave 0.4198 gram AgCl.

	Calculated for $C_3H_2Cl_2O_2$.	Found.
Cl	50:36	50.35

CRYSTALLINE FORM OF DICHLORACRYLIC ACID.



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[1] This Journal, **3**, 167; and Proceedings Amer. Academy, **16**, 206.

[2] Ann. Chem. u. Pharm. **203**, 83.

Monoclinic System.

Forms, [100] [001] [110] [$\bar{1}11$].

Elements: Clinodiagonal a=1.1865
Orthodiagonal b=1
Vertical Axis c=0.3637
Angle of Axes XZ=87° 32′

Angles between Normals.

	Observed.	Calculated.
111 and 111	=37° 54′	Fundamental angles.
$\bar{1}11$ " 001	=25° 8′	
$\bar{1}11$ " $\bar{1}00$	=71° 49′	
001 " 100	=87° 32′	87° 33′
$\bar{1}00$ " $\bar{1}10$	=49° 56′	49° 51′
110 " 110	=80° 6′	80° 18′

Although Wallach's dichloracrylic acid also crystallizes in the monoclinic system, the forms are totally unlike, and the difference between the two acids is therefore established.

XXIII.—ON THE RELATIONS BETWEEN DIBROMACRYLIC ACID AND TRIBROMPROPIONIC ACIDS.

By Henry B. Hill and Clement W. Andrews.

Nearly two years ago Michael and Norton[1] published a description of the tribrompropionic acid melting at 92° which was first mentioned by Linneman and Penl,[2] and which they obtained by the addition of bromine to the so-called β-monobromacrylic acid of Tollens and Wagner. In this paper they remarked that potassic hydrate attacked the acid readily in alcoholic solution, but they attempted no isolation of the dibromacrylic acid which was thus formed. They soon afterwards offered to relinquish the farther study of this acid, in case we felt interested to undertake its preparation and comparison with the dibromacrylic acid which one of us had already described. This kind offer was accepted, and we began the investigation at once. Although we had no difficulty in the isolation of a dibromacrylic acid which closely resembled that which had been made from mucobromic acid, still it was impossible to establish the identity of the two until the latter had been somewhat more carefully studied. In the meantime Mauthner and Suida,[1] in an article upon substituted acrylic and propionic acids, described again the preparation of the tribrompropionic acid melting at 92°, without having seen more than a brief notice of Michael and Norton's work. In this article they further showed that it might be converted by the action of potassic hydrate into a dibromacrylic acid, which, as they asserted, was identical with that which O. R. Jackson and one of us had obtained from mucobromic acid.[2] The only facts which they brought forward in support of this assertion were, the melting-point, 85°, the ready formation of malonic acid by the action of baric hydrate, and the anhydrous form of the lead salt. Since neither the melting-point nor the action of baric hydrate will discriminate between the two isomeric forms of dibromacrylic acid already known, and, moreover, since the lead salt of one of these two acids has never been described and of the other is not anhydrous, as one of us has recently shown, it is evident that these facts were wholly insufficient to characterize the acid in question. Our investigation of the same acid has shown us that their assertion, though unsupported by evidence, was accidentally correct.

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[1] This Journal, 2, 18.

[2] Berichte der deutsch. chem. Gesellsch. 8, 1098.

Dibromacrylic Acid, $C_3H_2Br_2O_2$.—In the preparation of the tribrompropionic acid necessary for this research we followed quite closely the method of Michael and Norton, although we did not consider it necessary to purify the dibrompropyl alcohol by distillation under diminished pressure before oxidation. For the conversion of the tribrompropionic acid into the corresponding dibromacrylic acid we have found it most advantageous to dissolve it in the calculated amount of a titrated solution of baric hydrate, and to allow the reaction to proceed at ordinary temperatures. After standing for several days the neutral or at most feebly alkaline solution was evaporated, and the acid extracted from the recrystallized barium salt thus obtained. Since this acid was found by preliminary trial to give a sparingly soluble acid potassium salt which crystallized in long silky needles, for further purification it was converted into this salt. After several recrystallizations from hot water, the acid was set free by the addition of hydrochloric acid and extracted with ether. The acid thus obtained crystallized in small oblique prisms readily soluble in alcohol, ether, and chloroform, more sparingly in benzol or carbonic disulphide. Under water the crystals melted at about 20° to a colorless oil which dissolved readily on heating. The acid dried over sulphuric acid melted at 85–86°, and gave on analysis percentages corresponding to the formula $C_3H_2Br_2O_2$.

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[1] Sitzungsberichte der kk. Akademie, Wien, **83**, 273.

[2] This Journal, **3**, 106; and Proceedings Amer. Acad. **16**, 192.

I. 0.7497 gram substance gave on combustion 0.4341 gram CO_2 and 0.0673 gram H_2O.

II. 0.2863 gram substance gave 0.4691 gram AgBr.

III. 0.2093 gram substance gave 0.3432 gram AgBr.

Calculated for $C_3H_2Br_2O_2$.		Found.		
		I.	II.	III.
C	15.65	15.79	...	...
H	0.87	1.00	...	...
Br	69.56	...	69.72	69.84

The solubility of the acid we determined by neutralizing with baric carbonate an aqueous solution prepared according to the method of V. Meyer and determining by precipitation the barium dissolved.

I. 12.4640 grams of a solution saturated at 18° gave 0.3124 gram $BaSO_4$.

II. 12.2745 grams of a solution saturated at 18° gave 0.3091 gram $BaSO_4$.

According to these determinations the aqueous solution saturated at 18° contained the following percentages:

I.	II.
4.95	4.97

Baric Dibromacrylate, $Ba(C_3HBr_2O_2)_2.H_2O$.—The barium salt made by neutralizing a solution of the acid with baric carbonate crystallized in rhombic plates more or less irregular in form, which, when dried by exposure to the air, contained one molecule of water.

I. 1.3641 gram of salt dried over H_2SO_4 gave by precipitation 0.5195 gram $BaSO_4$.

II. 3.1482 grams of the air-dried salt lost at 110° 0.0933 gram H_2O; 0.8202 gram of the same air-dried salt gave by precipitation 0.3147 gram $BaSO_4$.

III. 1.7219 gram of salt dried over H_2SO_4 lost at 120° 0.0520 gram H_2O; 0.6769 of the same salt gave by precipitation 0.2555 gram $BaSO_4$.

Calculated for $Ba(C_3HBr_2O_2)_2.H_2O$.		Found.		
		I.	II.	III.
Ba	22.35	22.40	22.56	22.19
H_2O	2.94	...	2.96	3.02

For its further identification we determined its solubility in water at 18°.

9.2373 grams of a solution saturated at 18° gave by precipitation 0.2131 gram $BaSO_4$.

From this determination it follows that the aqueous solution saturated at 18° contained 5.89 per cent. of the anhydrous salt.

Calcic Dibromacrylate, $Ca(C_3HBr_2O_2)_2.3H_2O$.—The calcium salt crystallized in clustered needles which contained three molecules of water of crystallization when dried by exposure to the air.

I. 0.5761 gram of the air-dried salt lost at 80° 0.0535 gram H_2O.
II. 0.5101 gram of the air-dried salt lost at 80° 0.0491 gram H_2O.

Calculated for $Ca(C_3HBr_2O_2)_2.3H_2O$.		Found.	
		I.	II.
H_2O	9.78	9.29	9.63

0.4608 gram of the salt dried at 80° gave on ignition with H_2SO_4 0.1262 gram $CaSO_4$.

	Calculated for $Ca(C_3HBr_2O_2)_2$.	Found.
Ca	8.03	8.06

Potassic Dibromacrylate, $KC_3HBr_2O_2$.—The potassium salt was made from the acid by neutralization with potassic carbonate. It crystallized in leafy plates which were anhydrous.

0.6842 gram of the air-dried salt gave on evaporation with H_2SO_4 and ignition 0.2229 gram K_2SO_4.

	Calculated for $KC_3HBr_2O_2$.	Found.
K	14.58	14.62

A comparison of these results with those which one of us has presented in the preceding paper will be facilitated by the following table, which gives the mean of each series of results:

	Dibromacrylic Acid from	
	Mucobromic	Tribrompropionic
Melting point, ...	85.5–86°	85–86°
Aqueous solution 18°, per cent. acid, .	4.92	4.96
Barium salt, per cent. water, . . .	2.97	2.99
Barium salt solubility 18°, ...	5.91	5.89
Calcium salt, per cent. water, . . .	9.56	9.46

Since the identity of the dibromacrylic acid formed by the subtraction of hydrobromic acid from the tribrompropionic acid melting at 92° with that derived from mucobromic acid was thus established with precision, it seemed to us of interest to study a little more closely the tribrompropionic acid which this same dibromacrylic acid forms by the addition of hydrobromic acid. Mr. C. F. Mabery[1] had with one of us already proved that such an addition product could be formed, but it had been prepared solely from the impure acid melting at 83–84° and very little studied. We therefore at first undertook its preparation in larger quantity from pure acid melting at 85–86°.

Tribrompropionic Acid, $C_3H_3Br_3O_2$.—When dibromacrylic acid made by the action of baric hydrate upon mucobromic acid is heated with three or four times its weight of hydrobromic acid saturated at 0° for eight or ten hours at 100° the needle-like prisms disappear and are replaced by rectangular plates of the new tribrompropionic acid. With the pure acid no carbonization such as had been noticed in working with the impure acid was observed even at 120°, and we therefore usually allowed the addition to proceed at this higher temperature, since the reaction was then completed in a shorter time. The tubes opened without marked pressure, and the crystalline product, separated from the acid mother-liquors by filtration upon a perforated platinum cone, was dried upon porous tiles. When treated in this way the dibromacrylic acid gave about its own weight of crude tribrompropionic acid. The acid can readily be purified by recrystallizing it successively from ligroin and carbonic disulphide. The use of carbonic disulphide causes considerable loss, but with ligroin alone we failed to obtain as high a melting-point. After several recrystallizations the acid showed a constant melting-point, and gave on analysis the required percentages.

I. 1.0329 gram substance dried over H_2SO_4 gave on combustion 0.4446 gram CO_2 and 0.0994 gram H_2O.

II. 0.2184 gram substance gave 0.3963 gram AgBr.

III. 0.1938 gram substance gave 0.3525 gram AgBr.

	Calculated for $C_3H_3Br_3O_2$.	Found.		
		I.	II.	III.
C	11.57	11.74	...	...
H	0.96	1.07	...	...
Br	77.17	...	77.29	77.39

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[1] This Journal, **3**, 116; and Proceedings Amer. Acad. **16**, 197.

This tribrompropionic acid is very soluble in alcohol or ether, somewhat less soluble in chloroform, carbonic disulphide, benzol, or ligroin. It dissolves freely in hot water, but is quite rapidly decomposed on boiling with the formation of hydrobromic acid. From the hot aqueous solution the acid crystallizes on cooling in pearly scales. Repeatedly recrystallized from carbonic disulphide, the acid melts at 118°.

Argentic Tribrompropionate, $AgC_3H_2Br_3O_2$.—Argentic nitrate added to a cold aqueous solution of the acid precipitates the silver salt in small clustered rhombic plates. On warming it with water argentic bromide is rapidly formed, but it may be dried over sulphuric acid without essential decomposition.

0.2901 gram of the salt dried over H_2SO_4 gave by precipitation with HBr 0.1316 gram AgBr.

	Calculated for $AgC_3H_2Br_3O_2$.	Found.
Ag	25.83	26.05

The barium and calcium salts were readily soluble in water, and their solution could not be warmed without the instantaneous formation of bromide. Even on evaporating their solutions at ordinary temperatures over sulphuric acid *in vacuo* the barium salt was almost wholly decomposed; the calcium salt was apparently somewhat more stable, for it was thus obtained in dendritic needles, although the mother-liquor contained calcic bromide. Since the air-dried salt lost nothing over sulphuric acid and was decomposed by heat, the water of crystallization could not be directly determined. It gave, however, a percentage of calcium agreeing closely with that required by two molecules of water.

I. 1.1087 gram of the air-dried salt gave on ignition with H_2SO_4 0.2179 gram $CaSO_4$.

II. 0.7279 gram of the air-dried salt gave on ignition with H_2SO_4 0.1425 gram $CaSO_4$.

	Calculated for $Ca(C_3H_2Br_3O_2)_2.2H_2O$.	Found.	
		I.	II.
Ca	5.75	5.78	5.76

We were unable to prepare other salts.

Dibromacrylic Acid.—The ready decomposition of the tribrompropionic acid made it seem desirable to isolate and identify the dibromacrylic acid which was thus formed. For this purpose we dissolved pure tribromproprionic acid, melting at 118°, in water, and added from a burette a titrated solution of baric hydrate. So rapid was the action that an alkaline reaction could not be maintained until nearly one molecule of baric hydrate had been added for each molecule of the acid. When the calculated amount of baric hydrate had been added the solution was allowed to stand for half an hour, and then but a trace of baric carbonate could be precipitated with carbonic dioxide. Ether extracted from the acidified solution a crystalline acid melting at 85–86°, which gave on analysis the percentage of bromine required by the formula $C_3H_2Br_2O_2$.

0.1979 gram substance gave 0.3240 gram AgBr.

	Calculated for $C_3H_2Br_2O_2$.	Found.
Br	69.57	69.66

The solubility of the acid in cold water was determined by the method of V. Meyer.

I. 10.7793 grams of a solution saturated at 18° gave on neutralization with baric carbonate and precipitation 0.2908 gram $BaSO_4$.

II. 7.7354 grams of a solution saturated at 18° gave 0.1940 gram $BaSO_4$.

According to these determinations the aqueous solution of the acid saturated at 18° contained the percentages:

I.	II.
5.32	4.95

Baric Dibromacrylate, $Ba(C_3HBr_2O_2)_2.H_2O$.—By neutralizing the acid with baric carbonate, or more conveniently by the direct evaporation of the solution obtained by the action of baric hydrate upon tribrompropionic acid, we obtained the barium salt in leafy rhombic plates which, when dried over sulphuric acid, contained one molecule of water.

I. 1.1489 gram of the salt dried over H_2SO_4 lost at 100-105° 0.0335 gram H_2O.

II. 1.5158 gram of the salt dried over H_2SO_4 lost at 105–110° 0.0457 gram H_2O, and gave on precipitation 0.5790 gram $BaSO_4$.

	Calculated for $Ba(C_3HBr_2O_2)_2.H_2O$.	Found.	
		I.	II.
Ba	22.35	...	22.46
H_2O	2.94	2.92	3.02

Calcic Dibromacrylate, $Ca(C_3HBr_2O_2)_2.3H_2O$.—The calcium salt crystallized in radiating needles which contained when air-dried three molecules of water.

0.9444 gram of the air-dried salt lost at 100–105° 0.0906 gram H_2O, and gave on ignition with H_2SO_4 0.2332 gram $CaSO_4$.

	Calculated for $Ca(C_3HBr_2O_2)_2.3H_2O$.	Found.
Ca	7.25	7.26
H_2O	9.78	9.59

These results are sufficient to prove that this dibromacrylic acid is identical with the one already studied, as a comparison of the mean results given in the following table will show:

	Dibromacrylic Acid from Mucobromic	Dibromacrylic Acid from Tribrompropicnic
Melting point, ...	85.5–86°	85–86°
Aqueous solution saturated at 18°, per cent. acid,	4.92	5.12
Barium salt, per cent. water, . . .	2.97	2.97
Calcium salt, per cent water, . . .	9.56	9.56

ON THE DETERMINATION OF SO-CALLED REVERTED PHOSPHORIC ACID.

By Clifford Richardson.

The usual method for the determination of reverted phosphoric acid depends upon the solubility of dicalcic phosphate and insolubility of tricalcic phosphate in a solution of neutral citrate of ammonia of a specific gravity of 1.09. With the introduction of superphosphates made from mineral sources great dissatisfaction has arisen with this method on the part of the manufacturers, who claim that the oxalate method, which was condemned by Fresenius, is the only one suited to their class of fertilizers.

The minerals, Navassa phosphate, South Carolina rock, &c., from which these superphosphates are manufactured, contain considerable amounts of iron, which causes a speedy reversion of the phosphoric acid which has been made soluble by sulphuric acid; but in this form, although considered by the producers as "reverted phosphoric acid," and as such possessed of a high commercial value, it is not apparently sufficiently soluble in citrate, employed in the usual manner, to be given as such in the results of the analyses. On this account the use of the oxalate method is demanded.

With a view of showing the varying action of oxalate of ammonia on this class of phosphates, both in their natural and manufactured conditions, the following determinations have been made nearly according to a scheme proposed by a committee appointed at the convention of agricultural chemists in Cincinnati in 1881.

THE VARYING ACTION OF OXALATE.

Wt. of sub. taken.	Wt. of Oxal. taken.	Volume of solut.	Time of digest.	Temp. of digest.	Precip. Phos. 25.		Navassa Acid, 12.		Navassa Acid, 39.		Navassa raw, 38.		So. Ca. Acid, 41.		So. Ca. raw, 40.		
						P_2O_5, undis.		P_2O_5, undis.		P_2O_5, undis.		P_2O_5, undis.		P_2O_5, undis.			P_2O_5, undis.
Total P_2O_5.					45.50	..	15.75	..	16.18	..	29.64	..	18.61	..	26.47	..	..
Soluble P_2O_5.					..	..	1.30	..	4.47	..	..	..	11.09	..	.	..	..
P_2O_5 Insol. in citrate.					..	..	6.50	..	6.25	..	..	..	5.90	..	..	..	..
Concentration of solution :																	
2.	5.	100.	60′	100°	..	..	..	4.35	3.05	3.37	..	24.78	..	3.52	..	..	22.30
2.	4.	100.	60′	100°	..	21.33	..	8.62	..	6.17	..	25.57	..	4.17	..	24.51	24.06
2.	2.	100.	60′	100°	..	27.88	..	10.63	..	7.94	..	27.18	..	5.62	..	..	24.64
2.	1.	100.	60′	100°	..	34.16	..	12.13	..	9.59	..	28.43	..	6.52	..	..	25.07
Ratio of solution to substance:																	
2.	2.	200.	60′	100°	..	..	..	..	..	7.54	..	26.57	..	5.77	..	..	24.39
2.	2.	100.	60′	100°	..	..	..	..	..	7.97	..	27.53	..	6.07	..	..	24.65
2.	2.	50.	60′	100°	..	..	..	..	..	8.84	..	28.00	..	7.35	..	..	24.74
Time of digestion :																	
2.	2.	100.	120′	100°	..	..	..	..	..	8.01	..	26.54	..	5.27	..	..	24.00
2.	2.	100.	60′	100°	..	..	..	..	..	..	..	27.09	..	5.98	..	..	24.37
2.	2.	100.	30′	100°	..	..	..	..	..	9.67	..	27.99	..	6.36	..	..	24.59
Temperature of digestion :																	
2.	2.	100.	60′	100°	..	..	..	4.35	..	7.88	..	27.18	..	5.84	..	..	24.08
2.	2.	100.	60′	100°c.d.	..	..	..	..	..	8.65	..	..	..	6.06	..	..	24.70
2.	2.	100.	60′	40°	..	..	..	9.46	..	10.56	..	28.67	..	6.81	..	..	24.98

In explanation of the table it must be said that the Navassa and South Carolina phosphates, with the exception of Navassa

No. 12, were supplied by the committee of the convention. The Navassa No. 12 was a specimen on hand for about six months in the laboratory of the Department of Agriculture, but from a like source as the others. The precipitated phosphate, which is introduced for comparison, was a commercial article, consisting of a mixture of di- and tricalcic phosphates. In the series for temperature, that marked 100° c.d. means that the flask was introduced into a copper water-bath containing three hundred cubic centimetres of boiling water and allowed to cool down for the time given.

There is also given a determination of the amount of phosphoric acid in the acid phosphates left undissolved on treatment with citrate in the usual way.

The obvious conclusions from these results are that the amount of phosphoric acid dissolved is entirely dependent on the time and temperature of digestion and concentration of solution; that while for any one fertilizer the citrate and oxalate methods may be made to agree by a suitable arrangement of conditions, no such arrangement will be suitable to even two fertilizers of one class, as is shown by the two samples of Navassa acid phosphates. The advantage, then, of oxalate over citrate does not appear except in its more energetic action, which could be also brought about in the use of citrate by an increase in the concentration of solution or of the time and temperature of digestion.

In bone superphosphates, owing to their simple composition, it is possible to arrange the conditions for the use of either citrate or oxalate to produce an accurate separation; but with the more complicated mineral superphosphates, in every sample of which the relative amount of iron changes, any such selection of proper conditions is impossible, and the only thing, until some better method can be discovered, will be to agree upon some mode of treatment of ferruginous phosphates which will, for the average, approach most nearly to the truth.

I am indebted to Mr. A. E. Knorr for a large number of the determinations in this paper.

WASHINGTON, *Jan.* 1882.

ON SOME DERIVATIVES OF p-OXY-m-TOLUIC ACID.

By R. W. Mahon.

This acid has been obtained by Tiemann and Schotten[1] and by Remsen and Iles,[2] and is known to have the structure represented by the formula $C_6H_3\begin{cases} OH & (1) \\ CH_3 & (2) \\ COOH & (4) \end{cases}$. It is most easily prepared according to the directions given by Remsen and Iles, viz. by oxidizing α-xylenesulphamide and fusing the resulting sulphaminetoluic acid with potassium hydroxide. I have prepared a considerable quantity of the acid, and studied a few of its derivatives which are described in this paper. The acid itself crystallizes in beautiful, long, colorless needles resembling salicylic acid. It contains half a molecule of water of crystallization. After drying at 120°, it fuses at 174.5° (corrected).

It was heated with ordinary concentrated nitric acid, for the purpose of converting it into a nitro-derivative. This operation, to be successful, must be conducted as follows: Quantities not exceeding a gram must be used, and boiled in the acid until perfectly dissolved. The action must then be instantly checked by plentiful dilution with water and rapid cooling. By working in this manner a series of yields were obtained, which consisted of fine glistening yellow needles. This material is extremely soluble in alcohol, especially when hot, yielding an intensely yellow solution, and from this solution it can be obtained in fine needles. Determination of the fusing point of this recrystallized product gave 86°–87° (corrected). This material is not very soluble in water, and is volatile with water vapor. In ether it is very soluble.

Calcium Nitro-oxytoluate, $(C_6H_2.OH.CH_3.NO_2.CO_2)_2Ca+4H_2O$. This was prepared by boiling the nitro-acid with finely pulverized calc spar. It is quite soluble in water, yielding an intensely red solution, and crystallizes in aggregations of fine gold yellow needles. These, when rendered anhydrous by heating, turn to an orange color, and the anhydrous salt is slightly hygroscopic. The salt explodes when heated.

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[1] Berichte der deutschen chemischen Gesellschaft, **11**, 767.

[2] This Journal, **1**, 32.

I. 0.2999 gram salt lost 0.0429 gram water of crystallization.
II. 0.1753 gram salt gave 0.0453 gram $CaSO_4$.

	Calculated.		Found.	
			II.	II.
$C_{16}H_{12}N_2O_{10}$	392	77.77	...	...
Ca	40	7.94	...	7.60
$4H_2O$	72	14.29	14.31	...
		100.00		

Barium Nitro-oxytoluate, $(C_6H_2.OH.CH_3.NO_2.CO_2)_2Ba+4H_2O$. This was prepared by boiling the acid with pure barium carbonate. It is quite soluble in water, yielding a red solution. From the solution it crystallizes in star-like aggregations of fine orange yellow needles. The anhydrous salt is of an intense crimson color, and somewhat hygroscopic. The salt explodes when heated.

I. 0.4031 gram salt gave up 0.0165 gram water of crystallization.
II. 0.2701 gram salt gave 0.1049 gram $BaSO_4$.

	Calculated.		Found.	
			II.	II.
$C_{16}H_{12}N_2O_{10}$	392	65.24	...	...
Ba	137	22.78		22.83
$4H_2O$	72	11.98	11.54	...
		100.00		

When the crystals of the nitro-acid are heated in water, part dissolves, and an oil is formed of a brownish yellow color. This oil is difficult to get into solution, and it was at first thought that there were two products formed when nitric acid acts on oxytoluic acid. That the crystals, and the oil, which is a solid yellow mass when cooled, are the same substance, was proved by the identity of their fusing points. Both the oil and the crystals dissolve in ammonia, yielding a red solution, which contains the ammonium salt of the nitro-derivative. Caustic soda added to this solution causes the evolution of ammonia. Hydrochloric acid re-precipitates the nitro-acid. This ammonium salt crystallizes out of solution in fine yellow needles, which cover the vessel in arborescent shapes. It turns to an orange color when rendered hygroscopic, and explodes when more strongly heated. The sodium salt also crystallizes in fine needles. These are of an orange color, and turn to a redder tint when heated. This salt also is explosive. Both the sodium and the ammonium salt are quite soluble in water. When the nitro-acid is thrown down by the addition of a stronger acid to a solution of one of its salts it is pure white, but it rapidly turns yellow. All the salts, as well as the acid itself, have marked tinctorial power.

Johns Hopkins University, *May*, 1882.

NOTE ON THE AMMONIA-PROCESS FOR WATER ANALYSIS.

By Charles W. Marsh.

The present article contains the results of some investigations in connection with a systematic examination and comparison of various methods of water analysis. Among other questions presented for examination was that of the possible loss of volatile organic matter during the evaporation and boiling of water, necessitated by the ammonia and other processes. At the suggestion of Prof. Cornwall the series of experiments in Table I was begun last fall. After the experiments had been nearly completed, a copy of a " Report on a Peculiar Condition of the Water of Boston in November, 1881," by Prof. Ira Remsen, was received, in which it was found that Prof. Remsen had already anticipated the results here given in his report, in which he says : " Another fact which came out in the examination of the Baltimore water was this : When free and 'albuminoid ammonia' were determined by the method already described, the amounts of the two added together were found to be considerably smaller than the total ammonia found when the oxidizing mixture was added at the beginning of the operation, before the water was boiled. This learly indicated that in the first stage of the process, as usually onducted, there passed over with the free ammonia some nitroenous substance capable of yielding ammonia with permanganate f potash. As this distillate had a strong odor, something like the cucumber odor,' the suggestion was made that the odor of the ater was due to the presence of some volatile nitrogenous subtance, the special nature of which could not be determined. The xamination of the Farm-pond water confirms this idea. One xample will make this clear, and will suffice : a specimen of Farm-ond water gave, when examined in the usual way, 0.034 free and .274 albuminoid ammonia, making a total of 0.308 parts of mmonia in 1,000,000 parts of water. When the same water was reated at the outset with the oxidizing mixture, it gave a total of .506 parts of ammonia. There remains here the difference etween 0.308 and 0.506 to be accounted for, or two-fifths of the otal. The material capable of yielding this lost ammonia was ndoubtedly lost in the distillations of the water for free ammonia, nd it must hence be a volatile nitrogenous substance."

The analyses in Table I may still prove of interest, both as erifying his statement and illustrating the great variability in the roportion of organic matter which may thus be lost. Twenty-six nalyses were made on different waters, proceeding in the followng manner : The analysis for free and albuminoid ammonia was ade as Wanklyn directs. Then 300 cc. were taken (the same uantity remaining in the retort when the permanganate of potash s added in the regular analysis), and 50 cc. of permanganate were dded, and three distillates of 50 cc. each were taken off and esslerized, and the whole calculated to one litre. This gave the otal ammonia. In only one case did the sum of the free and lbuminoid ammonia exceed the total ammonia. In three cases he results were identical, and in the other twenty-two the total mmonia was more than the sum of the free and albuminoid mmonia. In Table I in the first column is the free ammonia ; in he second the albuminoid ammonia ; in the third the sum of the wo ; in the fourth the total ammonia ; and in the fifth the differnce between the total ammonia and the sum of the free and lbuminoid ammonia.

TABLE I.

No.	Specimen.	Free Ammonia.	Albuminoid Ammonia.	Sum of Free Ammonia and Albuminoid Ammonia.	Total Ammonia.	Difference bet. Sum of Free Ammonia and Album'oid Am. and Total Am.
1	Well Water	.04	.15	.19	.29	.10
2	“ “	.05	.20	.25	.35	.10
3	“ “	.05	.10	.15	.18	.03
4	Cistern “	.01	.07	.08	.10	.02
5	“ “	.01	.06	.07	.07	.00
6	“ “	.09	.07	.16	.18	.02
7	Well “	.46	.07	.53	.56	.03
8	Canal “	.01	.20	.21	.21	.00
9	Distilled Water............	.36	.03	.39	.49	.10
10	Well Water	.01	.04	.05	.07	.02
11	“ “	.06	.08	.14	.16	.02
12	Spring “	.06	.08	.14	.15	.01
13	Surface “	8.10	1.75	9.85	10.12	.27
14	“ “	2.84	1.46	4.30	4.10	*.20
15	“ “	8.48	2.12	10.60	11.11	.51
16	Cistern “	.07	.08	.15	.18	.03
17	Well “	.02	.16	.18	.20	.02
18	“ “	.02	.07	.09	.10	.01
19	“ “	.01	.02	.03	.07	.04
20	Spring “	.01	.02	.03	.06	.03
21	Well “	.02	.03	.05	.06	.01
22	“ “	.11	.11	.22	.24	.02
23	“ “	.01	.04	.05	.10	.05
24	“ “	.16	.11	.27	.34	.07
25	“ “	.07	.08	.15	.20	.05
26	“ “	.04	.08	.12	.12	.00

The ammonia is expressed in parts per million.

It will be seen from the table that No. 14 was the only water where the sum of the free and albuminoid ammonia was greater than the total ammonia. This exceptional result may well be ascribed to the greater difficulty of accurately estimating the ammonia in highly colored nesslerized solutions, and to the fact that any actual errors of this kind were increased in calculating the results, since it was necessary to dilute the specimen very largely with water free from ammonia. In Nos. 5, 8 and 26 it appears that no volatile nitrogenous substance escaped, as will be seen from the last column. All the other waters show different amounts of gain of the total ammonia over the sum of the free and albuminoid ammonia, some slight and some comparatively very large. The results in the table conclusively prove that something escapes conversion into ammonia. Is this something which escapes condensation, or will it be found in the distillate? To decide this question 500 cc. of the water were boiled as usual to obtain a distillate of 200 cc., containing, according to Wanklyn, all the free ammonia. This distillate was redistilled with a proportionate amount of permanganate (33 cc.), and two distillates of 50 cc. each were obtained and nesslerized, the result being doubled to bring it up to one litre. This gave all the free ammonia and any ammonia which may come from the action of the permanganate on any condensible, nitrogenous, organic compound which had come over with the free ammonia. The ammonia from these two sources is given in the next to the last column Table II. In this table are the results of analysis on ten samples of water. In the first four columns the data are the same as in Table I. In the fifth column is the free ammonia and the ammonia which we have regained. In the sixth column is the sum of the albuminoid ammonia and the ammonia in the fifth column.

TABLE II.

No.	Specimen.	1 Free Ammonia.	2 Albuminoid Ammonia.	3 Sum of Free Am. and Alb. Am.	4 Total Ammonia.	5 Sum of Free Am. and Regained Am.	Sum of 2 and 5.
1	Well Water...	.04	.10	.14	.19	.06	.16
2	" " ...	.05	.10	.15	.16	.06	.16
3	" " .	.05	.08	.13	.17	.09	.17
4	" " ...	.04	.07	.11	.12	.06	.13
5	" " ...	.04	.07	.11	.12	.05	.12
6	" " ...	.05	.22	.27	.27	.05	.27
7	" " ...	.03	.12	.15	.17	.06	.18
8	" " ...	.04	.03	.07	.08	.05	.08
9	Cistern " ...	.05	.11	.16	.22	.08	.19
10	Well " .	.02	.08	.10	.15	.07	.15

The ammonia is expressed in parts per million.

It would appear that in the case, at least, of specimens Nos. 2, 3, 5, 6, 8 and 10, the excess of ammonia obtained where the whole of the water was distilled with the permanganate directly, over the sum of the free and albuminoid ammonia as usually obtained, was due to some volatile, condensible, nitrogenous compound, from which as much ammonia could be obtained by the action of boiling permanganate after its distillation from the original water, as before. In Nos. 1 and 9 the sum of the albuminoid ammonia and the ammonia from the redistillation is less than the total ammonia, hence some of the constituents escaped in the first distillation. In Nos. 4 and 7 the sum of the two ammonias in the sixth column is slightly greater than the total ammonia, which may be due to error of reading; at all events these two waters would show that all the ammonia was regained.

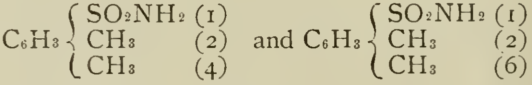
It is possible that the modification of the usual ammonia-process which is obviously suggested by the foregoing experiments may reconcile the differences now existing between the organic purity of water as determined by the ammonia-process, and the oxidation process with permanganate (Forchammer's and its modifications). Work in this direction is now going on.

John C. Green School of Science, Princeton, N. J., *March* 16, 1882.

ON THE BENZOYL DERIVATIVES OF THE XYLENE-SULPHAMIDES.

By R. W. Mahon.

It has been shown by the investigations of Remsen and Iles[1] and of Jacobsen[2] that the α- and β-sulphamides obtained from metaxylene have respectively the formulas



$$C_6H_3\begin{cases} SO_2NH_2 & (1) \\ CH_3 & (2) \\ CH_3 & (4) \end{cases} \text{ and } C_6H_3\begin{cases} SO_2NH_2 & (1) \\ CH_3 & (2) \\ CH_3 & (6) \end{cases}$$

As in the β-amide both methyl groups are in the ortho-position relatively to the sulphamide group, its conduct toward oxidizing agents is a matter of considerable interest. According to the law discovered by Professor Remsen, the validity of which has been established by a large number of investigations which have been carried on in this laboratory, it would appear that both the methyl groups ought to be protected when the amide is subjected to the influence of acid oxidizing agents. But it is stated by Jacobsen[1] that this amide conducts itself in the same way as the α-amide, yielding by oxidation with chromic acid a monobasic acid. His proofs are, however, wholly unsatisfactory, and Professor Remsen has shown[2] that the statement cannot be strictly correct. In view of the importance of the subject it seemed desirable to obtain a considerable quantity of the β-amide in pure condition and study its conduct carefully. Its separation from the α-amide by crystallization is extremely difficult, and but very small quantities can be obtained in this way. I have hence tried to effect the separation by the aid of the benzoyl derivatives. As Wolkow[3] has shown that the benzoyl derivatives of the sulphamides of toluene have markedly acid properties, it was hoped that the corresponding derivatives of xylene might yield salts which could be separated by crystallization.

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[1] This Journal, **1**, 32.

[2] Berichte der deutschen chemischen Gesellschaft, **10**, 1009.

Quantities of the mixed amides were heated with benzoyl chloride, in the proportion of their molecular weights, at a temperature of 150°–160°, in an oil-bath, until gas ceased to be given off. The black cakes left in the flasks were found to be insoluble in water and in ether; they dissolved easily in hot alcohol. The product was recrystallized from water and alcohol, and thus obtained in short colorless needles. Its fusing point was determined to be 149°–151° (uncorrected). This recrystallized product, when heated with alcoholic potash, yielded the simple α-xylenesulphamide. It also dissolved easily in ammonia, and from the ammoniacal solution, the addition of an excess of hydrochloric acid threw down a precipitate. To another portion of the ammoniacal solution, after the excess of ammonia had been driven off, barium chloride was added, causing the precipitation of a white crystalline material. This material proved to be a barium salt. Some of the acid precipitated from the solution of the ammonium salt was boiled with barium carbonate, and a barium salt was obtained in this way.

Estimations of barium and of water of crystallization were made in these materials, viz. that obtained by boiling with barium carbonate, and that precipitated by barium chloride from an ammoniacal solution of the material of fusing-point 149°–151°.

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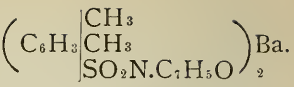
[1] Berichte der deutsch. chem. Gesellschaft, **11**, 893.

[2] This Journal, **1**, 32.

[3] Zeitschrift für Chemie, N. F. **6**, 577.

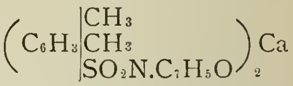
Barium α-xylenesulph-benzoyl-amide, 
$\left(C_6H_3\left|\begin{matrix}CH_3\\CH_3\\SO_2N.C_7H_5O\end{matrix}\right.\right)_2Ba.$
Crystallizes out of solution in fine colorless needles and is difficultly soluble in water.

1. 0.1207 gram salt lost no water at 155°, and gave 0.0391 gram $BaSO_4$.

2. 0.2734 gram salt lost no water at 125°, and gave 0.0886 gram $BaSO_4$.

3. 0.1349 gram salt lost no water, and gave 0.0438 gram $BaSO_4$.

	Calculated.		Found.		
			I.	II.	III.
$C_{30}H_{28}S_2N_2O_6$	576	80.79	...	...	...
Ba	137	19.21	19.66	19.05	19.09
		100.00			

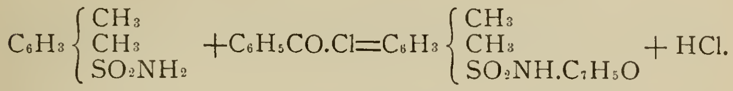
Calcium α-xylenesulph-benzoyl-amide, 
$\left(C_6H_3\left|\begin{matrix}CH_3\\CH_3\\SO_2N.C_7H_5O\end{matrix}\right.\right)_2Ca$
$+H_2O$. Crystallizes out of solution in fine colorless needles. It was prepared by boiling the acid with finely pulverized calc spar. This salt is difficultly soluble in water. The barium and calcium salts are about equally soluble. The calcium salt is soluble in alcohol and in ether. When recrystallized from alcohol it has the molecule of water of crystallization; this is true of the salt recrystallized from water also.

1. 0.31745 gram salt lost 0.009 gram water at 147°, and gave 0.06785 gram $CaSO_4$.

2. 1.0161 gram salt lost 0.0285 gram water at 150°, and gave 0.2129 gram $CaSO_4$.

	Calculated.		Found.	
			I.	II.
$C_{30}H_{28}N_2S_2O_6$	576	90.85	...	...
H_2O	18	2.84	2.84	2.80
Ca	40	6.31	6.29	6.16
		100.00		

Thus it will be seen that when the α-amide is heated with benzoyl chloride, a compound amide is formed, in which one atom of hydrogen in the amido group has been replaced by benzoyl, and in which the remaining hydrogen atom possesses acid properties. The reaction is represented by the equation—



$$C_6H_3\left\{\begin{array}{l}CH_3\\CH_3\\SO_2NH_2\end{array}\right. + C_6H_5CO.Cl = C_6H_3\left\{\begin{array}{l}CH_3\\CH_3\\SO_2NH.C_7H_5O\end{array}\right. + HCl.$$

When mixtures of the α- and β-amides (containing a large proportion of the latter) were heated with benzoyl chloride and the product dissolved in ammonia, the subsequent addition of an excess of hydrochloric acid caused the separation of a gummy mass, the gummy character of which was the more marked the more of the β-amide was present in the mixture acted on by the acid chloride. It was from such a gummy mass that by recrystallization from alcohol, the α-benzoylamide, a well characterized crystalline substance of fusing point 149°–151°, was obtained. After the removal of several crops of crystals of the α-benzoylamide from the alcoholic solution had been effected by stopping the evaporation of the solution at intervals, the subsequent evaporation to near dryness caused the deposition of a material of an oily nature, which solidified to a clear brownish yellow gum, holding crystals of the α-benzoylamide enclosed in it. From these experiments it is seen that when benzoyl chloride acts on a mixture of the α- and β-sulphamides of xylene, there are formed two products: α-benzoylamide, and an oil which is more soluble in alcohol than α-benzoylamide.

The following facts seem to indicate that the oily substance is the β-benzoylamide. It is easily soluble in ammonia or an alkaline carbonate, and from such solution an excess of hydrochloric acid precipitates the original oil; when boiled in water with pulverized calc spar and filtered, the addition of hydrochloric acid to a portion of the filtrate precipitates the original oil, and calcium is easily shown to be present; a solution which was shown to contain a barium salt is also similarly prepared with barium carbonate. If these various solutions be evaporated, an oil is in each case deposited, which is found to be insoluble in ammonia or alkaline carbonates; these being, as already suggested, probably salts of the compound amide. The oils, or gums, examined, especially the original gum, and the result of boiling that with calc spar, were found to themselves possess the property of dissolving the crystals of the α-amide, and a part of these crystals separated out on cooling. Quantities of oil holding apparently no crystalline material were allowed to stand for days over concentrated sulphuric acid, when a considerable crop of crystals made their appearance. All of the simple α- and β-amides at hand were now heated with benzoyl chloride in the proportion of their molecular weights, and at the temperature mentioned above (150°–160°). The material was divided into two parts, that consisting mostly of α-amide and that consisting mostly of β-amide; and these were worked up separately. By repeated crystallizations of the product from alcohol, the supposed β-benzoylamide was obtained in a condition of considerable purity. This purified product was boiled with finely pulverized calc spar. After filtering, the gummy calcium salt above mentioned was obtained from the filtrate, with some crystalline material, the calcium salt of the α-benzoylamide. This oily material was dissolved in water, in which it is difficultly soluble, and the addition of hydrochloric acid to its solution caused the separation of the β-benzoylamide. By further heating in water more crystals were mechanically separated. This process of mechanical separation having been several times repeated, the β-benzoylamide was obtained in a comparatively pure condition, although, owing to the solubility of the α in the β compound, not entirely so. Hence no attempt was made to analyze the salts. It was thought that nearly pure β-amide could probably be obtained from the purified oil. As the α-benzoylamide is decomposed readily by boiling with alcoholic potash yielding the simple amide quantitatively, the effect of this reagent was first tried on the β compound. As far as could be judged no effect was produced, certainly no β-sulphamide was obtained. It was then boiled with concentrated hydrochloric acid, without effecting its decomposition. The α-benzoylamide is also undecomposed by boiling with concentrated hydrochloric acid. Quantities of the β-benzoylamide were heated with concentrated hydrochloric acid in sealed tubes, without yielding the simple amide. When heated at 169° for several hours, with a large excess of concentrated hydrochloric acid, the gum entirely disappeared; but careful examination failed to detect any simple β-amide in the product. The action of concentrated sulphuric acid on the β-benzoylamide was also studied, but no decomposition into simple amide noticed. Owing to this extreme and unexpected stability of the β compound, the attempt to prepare the simple amide from the material employed in this investigation was unsuccessful. It must be said that notwithstanding the general properties of the oily product above described, its stability makes it appear doubtful whether it really was the β-benzoylamide. It may have been some other product of the action of benzoyl chloride on the β-sulphamide.

JOHNS HOPKINS UNIVERSITY, *May*, 1882.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

XII.—PROTECTION OF A GROUP CONTAINING TWO CARBON ATOMS.

BY IRA REMSEN AND W. A. NOYES.

That negative atoms or groups in the ortho-position relatively to methyl protect the latter from the influence of the oxidizing action of chromic acid may now be regarded as established. The questions naturally suggest themselves: (1) Can these same groups protect ethyl, propyl, and more complex residues? (2) How far does this protective influence extend? or, in other words, if larger residues than methyl are protected, what is the largest which can thus be protected? There are very few, if any, facts recorded which can aid us in forming a conclusion. The case described by von Gerichten[1] some time since, to which attention was called in an earlier paper of this series, has perhaps some bearing on the questions. This author obtained a chlorcymene by treating thymol with phosphorus pentachloride. In the product the chlorine atom should be in the ortho-position relatively to the propyl group. By oxidation with nitric acid this chlorcymene yields an acid having the empirical formula of a chlor-propylbenzoic acid. It appeared probable that the formation of this acid might be explained by supposing that the chlorine protects the entire propyl group and that the para-methyl is transformed into carboxyl. Later, von Gerichten states that his acid is not chlor-propyl-benzoic acid, but that the carboxyl is in the propyl. The acid is, according to him,

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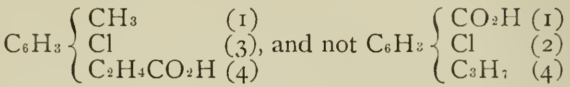
[1] Berichte der deutschen chemischen Gesellschaft, **11**, 365. 1719.



$$C_6H_3\begin{cases} CH_3 & (1) \\ Cl & (3), \\ C_2H_4CO_2H & (4) \end{cases} \text{and not } C_6H_3\begin{cases} CO_2H & (1) \\ Cl & (2) \\ C_3H_7 & (4) \end{cases}$$

One of us has already criticized the paper of von Gerichten and shown that his view is very improbable. At the same time his statements have not been disproved, nor has he in any way modified them since. There is one other case of a somewhat similar character which should be referred to. Aschenbrandt[1] has shown that when para-diethyl-benzene is treated with nitric acid, two effects are produced—a nitro group is introduced into the compound and one ethyl group is changed to carboxyl. It is impossible, however, from the experiments described to determine (1) whether the nitro group enters the hydrocarbon first, and the nitro product is then oxidized; (2) whether the oxidation first takes place, and the nitro group then enters the acid; and (3) what the structure of the nitro-ethyl-benzoic acid is. It appears probable that the nitro group first enters the hydrocarbon, and that then oxidation takes place. But the formation of nitro-ethyl-benzoic acid under the circumstances described would not prove that the nitro-group protects the ethyl, for the reason that, as a rule, nitric acid has the power to oxidize only one of two paraffin residues contained in an aromatic hydrocarbon, whether a negative group is present or not. So, also, whatever may be the nature of von Gerichten's acid, it must be borne in mind that it is formed by oxidizing with nitric acid, and, as yet, very little is known in regard to the action of this agent. The main question at present is simply: How does *chromic acid* act on compounds in which there are negative groups in the ortho-position relatively to paraffin residues of greater complexity than methyl?

It is not an easy matter to get substitution-products which furnish the necessary conditions for an investigation of the kind proposed. It appears to be highly probable that, when negative groups enter aromatic hydrocarbons in which there are two paraffin residues of different composition, the substitution takes place in the ortho-position relatively to the residue containing the smaller number of carbon atoms. Thus, when cymene, $C_6H_4\begin{cases} CH_3 \\ C_3H_7 \end{cases}$, is treated with bromine, chlorine, nitric acid, or sulphuric acid, the product in each case contains the substituting atom or group in the ortho-position relatively to methyl. Paterno,[1] Spica[2] and Claus[3] have indeed shown that when sulphuric acid acts on cymene, the second possible sulphonic acid, viz.

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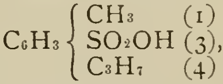
[1] Berichte der deutschen chemischen Gesellschaft, **12**, 1304.



$$C_6H_3\left\{\begin{array}{ll} CH_3 & (1) \\ SO_2OH & (3) \\ C_3H_7 & (4) \end{array}\right.$$

in which the sulpho-group is ortho relatively to propyl, is formed, but, under ordinary circumstances, in very small quantity. The experiments of Morse and Remsen[4] also seem to indicate that, when para-ethyl-toluene is treated with bromine, that product is formed in which the bromine is ortho relatively to methyl. In order, therefore, to secure a substance containing a substituting group in the ortho-position relatively to a residue more complex than methyl, we started from para-diethyl-benzene. This was converted into the sulphonic acid. From the acid the corresponding amide was prepared, and this was subjected to oxidation.

In the preparation of diethyl-benzene the directions of Aschenbrandt[5] were followed. The greatest precautions were taken, but still the yield was small. The reaction is by no means as clean as that which takes place between dibrom-benzene and methyl iodide. We used in some experiments ethyl bromide, in others ethyl iodide. The yield was somewhat better when the former was used. Most of the ether used had been standing in contact with metallic sodium for nearly a year, and had previously served in the synthetical preparation of para-xylene. The largest amount of bibrom-benzene used in any one experiment was 50 grams. This was mixed with about one-fourth more than the theoretical quantity of ethyl bromide or iodide. The mixture was kept cool by ice. The reaction took place slowly and required about twenty-four hours for its completion. We obtained only about thirty grams of the desired product instead of one hundred and seventy grams required by theory. The hydrocarbon boiled at 183° (uncorrected). Aschenbrandt[6] gives 181°–182°, and Fittig[7] 178°–179° as the boiling point.

[1] Gazetta chimica italiana, **4**, 115.

[2] Berichte der deutschen chemischen Gesellschaft, **14**, 652.

[3] *Ibid.* **13**, 901, 2044; and **14**, 2139.

[4] This Journal, **1**, 138.

[5] Berichte der deutschen chemischen Gesellschaft, **12**, 1303.

[6] *Loc. cit.*

[7] Annalen der Chemie, **144**, 285.

Sulphamide of Diethyl-benzene.

About twenty grams of the hydrocarbon were treated with 75 to 100 grams of fuming sulphuric acid. Solution took place readily with considerable evolution of heat. To complete the action the whole was finally heated for a short time on a water-bath. On diluting with water, neutralizing with pure barium carbonate, filtering and concentrating to about 500 cc., a quantity of the barium salt crystallized out. This was recrystallized and analyzed.

0.3600 gram of the air-dried salt lost 0.401 gram H_2O at 150° and gave 0.1316 gram $BaSO_4$.

	Calculated.		Found.
$(C_{10}H_{13}SO_3)_2$	426	67.09	...
Ba	137	21.57	21.49
4 H_2O	72	11.34	11.14

The solubility of the salt was determined by Victor Meyer's method.

1.1887 gram of a solution saturated at 23° gave 0.0577 gram of the anhydrous salt dried at 140°.

100 parts of water at 23° dissolve 5.1 parts of the anhydrous salt.

The formula of the salt is seen to be $\left\{ C_6H_3 \left\{ \begin{matrix} (C_2H_5)_2 \\ SO_2O \end{matrix} \right\}_2 \right. Ba + 4H_2O$. It crystallizes well in small leaflets with a beautiful pearly lustre. The water of crystallization is given off almost entirely at 102°. Fittig, who has prepared the salt, does not mention the water of crystallization nor the fact that the salt crystallizes. Probably he had but a very small quantity of it in impure condition, as it crystallizes very readily when pure.

The barium salt was converted into the potassium salt, and the latter evaporated to dryness and converted into the amide by the usual reactions. The conversion of the chloride into the amide took place with difficulty. Prolonged heating with concentrated aqueous ammonia was necessary, while ammonia gas was passed through the liquid. The amide was easily purified by recrystallization from water, in which it is difficultly soluble. It fuses under water below the boiling point. It crystallizes in small leaflets and is colorless. It fuses at 97.5° (corrected). The analyses gave results as follows:

I. 0.01565 gram of the amide gave 0.001045 gram N. (Frankland's method.)

II. 0.2167 gram gave 0.01469 gram N.
III. 0.1011 gram gave 0.1131 gram $BaSO_4$. (Liebig's method.)

Calculated.			Found.		
			I.	II.	III.
C_{10}	120	56.34	...	...	...
H_{15}	15	7.04	...	...	...
N	14	6.58	6.68	6.78	...
S	32	15.02	...	...	15.36
O_2	32	15.02	...	...	...

The method of preparation and the results of the analyses show that the substance is $C_6H_3\left\{\begin{array}{ll} C_2H_5 & (1) \\ SO_2NH_2 & (2) \\ C_2H_5 & (4) \end{array}\right.$

Oxidation of Para-diethyl-benzene-sulphamide.
Sulphamine-ethyl-benzoic acid.

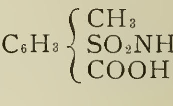
The amide was treated with chromic acid in these proportions: 24 grams of potassium pyrochromate, 36 grams of concentrated sulphuric acid, diluted with three volumes of water, and 5 grams of the amide. The whole was heated over a small free flame for about an hour. On cooling, a well crystallized substance was deposited. The whole was diluted with water and filtered. The acid remaining in the filter was well washed out, and then treated with dilute sodium carbonate, in order to separate the acid from some unchanged amide. The solution was boiled and evaporated down to a small volume, when the amide crystallized out. This was filtered off, and the acid precipitated from the filtrate by the addition of hydrochloric acid. By dissolving in water, boiling with animal charcoal, filtering, and allowing to cool, the acid was obtained in beautiful, long, colorless needles. This is, however, not perfectly pure, as the amide is much more soluble in an alkaline than in an acid solution. The acid was finally obtained in perfectly pure condition by preparing the barium salt and recrystallizing this. It fuses at 261°–262° (corrected), at the same time undergoing slight decomposition.

The analyses gave the following results:

I. 0.0141 gram gave 0.000906 gram N (Frankland's method).
II. 0.1069 gram gave 0.1101 gram $BaSO_4$ (Liebig's method).

	Calculated.		Found.	
			I.	II.
$C_9H_{11}O_4$	183	79.91	...	...
S	32	13.98	...	14.14
N	14	6.11	6.48	...
	229	100.00		

It is at least evident from these results that both the ethyl groups have not been oxidized to carboxyl. Disregarding any preconceived notions concerning protection, there are four possible products to be decided between. These are:

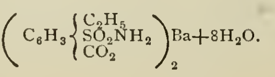
(1) $C_6H_3\left\{\begin{array}{l}COOH\\SO_2NH_2\\COOH\end{array}\right.$; (2) $C_6H_3\left\{\begin{array}{l}CH_2COOH\\SO_2NH_2\\COOH\end{array}\right.$; (3)  $C_6H_3\left\{\begin{array}{l}CH_3\\SO_2NH_2\\COOH\end{array}\right.$;

and (4) $C_6H_3\left\{\begin{array}{l}C_2H_5\\SO_2NH_2\\COOH\end{array}\right.$. Formula (1) requires 5.71 per cent. N and 13.06 per cent. S; and formula (2) still less, so that these are excluded at once. Of the two others (3) requires 6.51 per cent. N and 14.88 per cent. S. When we consider the difficulties involved in making accurate estimations of nitrogen and sulphur in substances of the kind with which we are dealing, the results obtained by us can hardly be considered as positive evidence against formula (3), though they agree much better with those required by formula (4). Finally, the barium salt was prepared, and every precaution taken to secure it in a state of perfect purity. It is easily soluble in water, and crystallizes in needles, which we were not able to free from a slight yellow color. The dried salt was finely pulverized, and treated with a little strong alcohol for the purpose of dissolving any traces of the original amide. It was then washed on the filter with alcohol, dried, and recrystallized from water. It crystallized as before in fine concentrically grouped needles, with a slight yellow color. Two analyses were made with the following results:

I. 0.1984 gram of the air-dried salt lost 0.0388 gram H_2O at 150°, and gave 0.0624 gram $BaSO_4$.

II. 0.2748 gram air-dried salt lost 0.0512 gram H_2O at 150°, and gave 0.0876 gram $BaSO_4$.

The results with the water of crystallization do not agree, as will be seen:



	Calculated for $\left(C_6H_3\left\{\begin{array}{l}C_2H_5\\SO_2NH_2\\CO_2\end{array}\right.\right)_2Ba+8H_2O.$	Found.	
		I.	II.
H_2O	19.54	19.56	18.63

The salt used for the second analysis had stood for twenty-four hours in a very dry and warm room, and had evidently lost some of its water, as its appearance indicated slight efflorescence. The barium estimations, however, calculated on the basis of the anhydrous salt, agree excellently, and leave no room for doubt regarding the composition of the salt.

		Found.	
Calculated for $\left(C_6H_3\begin{cases}C_2H_5\\SO_2NH_2\\CO_2\end{cases}\right)_2Ba.$		I.	II.
Ba	23.10	23.00	23.03

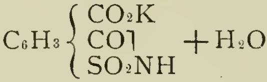
It is clear then that the salt is derived from sulphamine-ethylbenzoic acid, $C_6H_3\begin{cases}C_2H_5\\SO_2NH_2,\\COOH\end{cases}$ and not from sulphamine-toluic acid $C_6H_3\begin{cases}CH_3\\SO_2NH_2.\\COOH\end{cases}$ The anhydrous barium salt of the latter acid requires 24.25 per cent. barium.

The presence of the sulphamine group prevents the oxidation of the ethyl group by chromic acid, just as it has been found to prevent the oxidation of the methyl group in the many cases studied.

While from the experiments described the fact is established that the sulphamine group exerts a protective influence on the ethyl group, they do not show whether these two groups are in the ortho-position relatively to each other or not. Analogy indicates that they do stand in this relation, but it is desirable to furnish independent proof of the fact.

The sulphamine group must be either in the ortho- or the meta-position relatively to the carboxyl. If it were in the ortho-position, the substance obtained by oxidation should belong to the class called sulphinides, and have the formula $C_6H_3\begin{cases}C_2H_5\\ \left.\begin{matrix}SO_2\\CO\end{matrix}\right\}NH.\end{cases}$ This statement is based on the fact that in every case known in which the sulphamine and carboxyl groups are in the ortho-position relatively to each other, the corresponding sulphinide is formed. The analyses of the free acid given above, though they are perhaps not conclusive, indicate that it is the acid and not the sulphinide. The latter requires 6.64 per cent. N and 15.17 per cent. S; while the results found are 6.48 per cent. N and 14.14 per cent. S. As far as our experiments are concerned the question as to the relative position of the sulphamine and carboxyl groups must be regarded as to some extent an open one, though, as will be clear, there is a strong probability in favor of the view that the relation is that which is commonly called ortho.

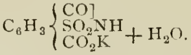
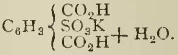
Oxidation of Sulphamine-ethyl-benzoic Acid with Potassium Permanganate.

It has been shown by previous experiments[1] that when sulphamine-para-toluic acid is oxidized with potassium permanganate in slightly alkaline solution, terephthalic sulphinide, or rather its potassium salt,  $C_6H_3\left\{\begin{array}{l}CO_2K\\ CO]\\ SO_2NH\end{array}\right. + H_2O$, is formed. The same product should be formed from the sulphamine acid above described.

One gram of the acid was dissolved in a slight excess of potassium hydroxide and added to a solution of six grams of potassium permanganate in 100 cc. of water. The mixture was heated for twelve hours on the water-bath. The permanganate was completely decolorized. The oxides of manganese were filtered off, the filtrate evaporated to about 75 cc., and acidified with hydrochloric acid. After standing for some time, a white substance crystallized out in fine needles. Analysis I, given below, was made with this portion. On evaporating the mother-liquor and allowing it to cool, a second portion crystallized out. This was filtered off and well washed with water. This was used for analysis II.

I. 0.2795 gram of portion I lost 0.0164 gram H_2O at 150°, and gave 0.0821 gram K_2SO_4. This salt gave a marked reaction for nitrogen with soda-lime.

II. 0.1269 gram of portion II lost 0.0075 gram H_2O at 150°, and gave 0.0365 gram K_2SO_4. This salt gave only a slight reaction for nitrogen with soda-lime.

	Calculated for  $C_6H_3\left\{\begin{array}{l}CO]\\ SO_2NH\\ CO_2K\end{array}\right. + H_2O.$	Found. I.	 II.	Calculated for  $C_6H_3\left\{\begin{array}{l}CO_2H\\ SO_3K\\ CO_2H\end{array}\right. + H_2O.$
K	13.81	13.17	12.92	12.94
H_2O	6.36	5.87	5.91	5.96

The results of the analyses together with the nitrogen tests show that the first specimen contained some of the nitrogenous substance, but that the second specimen was nearly pure mono-potassium sulpho-terephthalate. Its properties were the same as those of this salt as given by Remsen and Hall.[1] Although we worked under the same conditions as they did, we plainly obtained a mixture of the two products. This may possibly be explained by the fact that in the case of the ethyl compound a quantity of carbonic acid is formed by the oxidation of a part of the ethyl group, and Fahlberg[2] has shown that in a similar case the presence of carbonic acid was sufficient to prevent the formation of the sulphinide and cause the formation of the corresponding sulphonic acid. The small quantity of material at our disposal prevented us from following this inquiry farther.

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[1] See Remsen and Hall, this Journal, 2, 58.

In order to obtain direct evidence with regard to the position of the negative group in a case similar to that discussed above, we started in another experiment from the mono-bromine derivative of diethyl-benzene. This was readily made, though the lack of sufficient material made its purification impossible. It was oxidized with chromic acid and yielded a difficultly soluble acid. The barium and calcium salts also proved to be difficultly soluble. The acid, purified as far as possible, was mixed with an equal weight of quick-lime, and distilled in the hope that the corresponding brom-ethyl-benzene might be obtained, and that the oxidation of this with potassium permanganate would enable us to decide whether it was an ortho- or a meta-compound. The experiment was not successful. It will be repeated at the earliest opportunity. Experiments are now in progress with the object of determining whether an acid group can fully protect a residue as large as propyl from the oxidizing action of chromic acid.

JUNE, 1882.

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[1] *Loc. cit.*

[2] This Journal, 2, 131.

ON THE OCCURRENCE OF A NEW FAT ACID IN THE NUT OF THE CALIFORNIA BAY TREE.

By J. M. Stillman and E. C. O'Neill.

The peculiar properties and composition of the essential oil o the California laurel or bay tree, *Umbellularia Californica* (otherwise known as *Oreodaphne Californica*, *Tetranthera Californica*, or *Laurus Californica*), as investigated by one of us,[1] made it seem of interest to investigate the fat occurring in the seed or nut of the tree. The tree in question is one of the most widely distributed as well as one of the largest and handsomest of the valley trees o California. It is evergreen; its wood is much used as an ornamental wood in cabinet-work. The leaves when crushed possess a powerful and penetrating odor, which, however, when not too strong is very pleasant. The same pleasant odor, but fainter, is present in the wood when freshly cut, even if the wood is seasoned.

The fruit consists of a berry something larger than the olive and of about the same shape, enclosing a smooth seed something smaller than an olive. This seed or nut has a thin but hard shell and a large dry kernel. The fruit grows abundantly at the proper season, December and January, and falls when ripe, at which time it can be easily gathered in large quantities. On the banks and in the beds of streams, where the tree seems to thrive best, we had no difficulty in collecting a water-bucket full of the fruit in about half an hour.

The nuts, divested of their fleshy husks and the shells, were thoroughly ground in a mortar, and then digested with pure ether in an apparatus which was essentially a modification of Drechsel's apparatus for the quantitative estimation of fats.[2] By this means, with little labor and a minimum quantity of ether, the entire amount of fat was readily extracted. The ether was then distilled, leaving the pure fat. By this process we obtained from one charge of 392 grams of nuts, 231.5 grams of fat, or a fat-content of 59 per cent. The fat thus obtained solidified on cooling to a hard tallowy mass, nearly white, melting at from 31° to 32° C., and of specific gravity 0.925 at 31° C. when melted. Its taste is disagreeable, producing in the throat irritation, possibly due to a certain quantity of free fat acid in the fat. The fat is readily soluble in ether and benzol, but very slightly in alcohol.

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[1] This Journal, **2**, 38.

[2] Journal für praktische Chemie, **15**, 1877, 350, plate II.

A considerable quantity of the fat was then saponified with strong caustic potash, and the resulting clear soap solution decomposed by dilute hydrochloric acid. The clear oily layer which separated on the surface was washed several times by shaking with hot water, separated and dried. On cooling it composed a white, dry, tallowy mass, of faint odor when cold, but when heated giving off a peculiarly disagreeable, irritating odor. Its taste is disagreeable, irritating the throat. Its melting point was found to vary from 31° to 34° C. with different preparations.

An analysis of the acid mass as thus set free, purified and dried, gave

$$C = 71.24$$
$$H = 11.91.$$

To ascertain whether the acid so prepared was homogeneous or composed of a mixture of acids, a fractional precipitation was undertaken. An alcoholic solution of the acid was treated with an alcoholic solution of magnesium acetate, the mixture saturated with ammonia and allowed to stand. Several successive fractions were removed in the course of a couple of days by filtration, of which the first fraction composed over one-fourth the entire mixture. The magnesium salts so obtained were decomposed, with hydrochloric acid, the fat acid washed repeatedly with hot water, and finally dissolved in alcohol and reprecipitated with water, and dried in the air-bath. The last two fractions separated, No. 6 and No. 7, were slightly brown, the others were white. The melting points of the fractions were as follows:

Fraction	1	2	3	4	5	6	7
Melting pt.	34°	34°	32°	31°	...	25°	21°

Presumably the fraction 1 would contain the acids of greatest molecular weight, and the last fractions those of lowest molecular weight. Hence elementary analyses of fractions 1 and 5 were undertaken, both of these being pure white, whereas 6 and 7 were slightly discolored. The results were as follows:

Fraction 1.

	I[1].	II.	III.	Calculated for $C_{11}H_{22}O_2$.
C	71.37	70.75	71.05	70.97
H	11.67	11.71	11.68	11.81

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[1] This one analysis was made before complete purification of the fraction, and gave a slight ash on combustion.

Fraction 5.

C	71.04
H	11.74

A silver salt of the acid was prepared and analyzed.

	Found.	Calculated for $C_{11}H_{21}AgO_2$.
Ag	36.90	35.86

With one exception the analyses seemed to indicate a slightly high carbon content. We therefore decided to employ the method of Krafft,[1] by distillation under diminished pressure, to purify the acid. A quantity of the fat acid was first distilled under a diminished pressure of about 160 mm. of mercury. A large proportion passed over at from 240°–250° C., mostly in the neighborhood of 249°. A second portion was collected separately, which passed over at from 250°–270°, most of it passing over below 260°. The appearance of both portions of the distillate was pure white on cooling, and the lower fraction especially presented a distinct crystalline character. These fractions were then submitted to fractional distillation at ordinary atmospheric pressure. The distillation commenced at about 260° C., and small portions were left in the flask at 300°, the greater quantity passing over, however, between 265° and 275°, and this portion was again subjected to fractional distillation. The boiling point seemed to lie between 270°–275° (uncorrected, or corrected by Kopp's formula 275°–280°). This portion boiling from 265°–275° was again subjected to distillation in diminished pressure, and the first two-thirds of the distillate taken. The boiling point indicated by this last distillation under a diminished pressure of 100 mm. was about 205°–208° (or corrected by Kopp's formula 208°–211°).

The melting points of the fractions obtained by the distillation under ordinary atmospheric pressure varied from 21° for the lowest fraction to 38° for the residue remaining in the flask; those portions of the distillate of most clearly crystalline character and most nearly constant boiling point melted at from 21° to 23°. To obtain a more accurate melting point we took:

(*a*) The fraction distilling from 270°–272° and melting at 21°, purified it by solution in alcohol and reprecipitation by water, and dried it at 110°. It then melted at 21.2°.

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[1] Berichte der deutschen chemischen Gesellschaft, **11**, 2219.

(*b*) A portion distilling at 272°–275° and melting at 22°. This was converted into a silver salt, and the acid set free from the silver salt by dilute nitric acid, and the acid thus set free was purified as above. It melted at 22.5°–22.8°.

(*c*) A portion of the last-mentioned distillate under diminished pressure. This melted at 21.2°.

In order to check the composition of these fractions, analyses of silver salts prepared from them and recrystallized from hot alcohol, were made. As the silver salts were reduced by boiling alcohol, we had some difficulty in getting specimens which, on drying from the alcohol, would not turn brown in the drying.

The silver salt prepared from (*a*) gave 36.40 per cent. Ag; calculated for $C_{11}H_{21}AgO_2 = 36.86$. This result was a little low, but the salt dried partially on the filter-paper and a few shreds of the filter-paper adhered to it, which is perhaps sufficient to account for the low result, the salt being small in quantity.

The silver salt of (*b*) gave $Ag = 36.77$ per cent.; (salt pure white when dry).

The silver salt of (*c*) gave

I. $Ag = 37.06$ (nearly pure white when dry).

II. $Ag = 37.21$ (brown on the edges when dry).

A silver salt was prepared from the residues remaining in the flask after the distillation under diminished pressure. Its analysis gave $Ag = 34.17$ per cent., showing a probable admixture of some higher acid or acids in the higher boiling fractions.[1]

Ethers.

The methyl ether was prepared by acting on a solution of the fat acid (as set free from the fat) in methyl alcohol, with dry hydrochloric acid. The liquid soon separated into two layers. When saturation was complete the flask was warmed on the sand-bath to expel the excess of alcohol and acid, the remaining liquid washed with water and dried over calcium chloride. The ether distilled over mainly from 240° to 250° C., and on the third fractional distillation indicated a boiling point of 244° to 246°; it constitutes a mobile liquid of pleasant odor.

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[1] Elementary analyses of the fraction denominated (*c*) above were attempted, but, owing to the quality of the gasoline in use at the time, it was found impossible to heat the combustion tube to a sufficient temperature, and the results were not accordant. The analysis made under most favorable circumstances in this respect gave $C = 70.55$; $H = 11.61$.

The ethyl ether was obtained in the same way by the use of absolute alcohol. On a third fractional distillation it passed over mainly from 248° to 258°, its boiling point apparently lying between 253° and 255°. A portion passing over at this latter temperature was subjected to elementary analysis.

Found.	Calculated for $C_{11}H_{21}(C_2H_5)O_2$
C 72.83	C 72.90
H 12.15	H 12.15

This also was a mobile colorless liquid of pleasant odor.

The amyl ether, prepared in a similar way from amyl alcohol, is also capable of distillation with but slight decomposition, boiling at about 295° C. It is a mobile liquid of agreeable odor.

It will appear evident, we think, from the above data, that a new acid of the acetic acid series constitutes the main portion of the fat under investigation. The designation which it seems most appropriate to apply to this acid is that taken from the now accepted name of the tree, viz. *Umbellulic acid.* There seems to be present, however, a certain quantity of some higher acid, possibly also a small quantity of some lower acid. The umbellulic acid is a white crystalline solid of peculiar taste, irritating the mucous membrane of the throat. This peculiar taste was noticed in the acid after distillation, after purification with alcohol and water, and also in the acid obtained from the decomposition of the silver salts. It does not seem probable, therefore, that the taste is due to mere impurities. The same taste is noticed in the fresh nut as well. The acid distills at ordinary atmospheric pressure without decomposition, giving a water-clear distillate, which solidifies on cooling to a white crystalline solid. Its melting point seems to be from 21° to 23° C., but small quantities of other acids perhaps raise the melting point appreciably above these figures. The boiling point, as noticed above, appears to be at from 275° to 280° (corrected according to Kopp's formula) at ordinary pressure, and at 208°–211° under a pressure of 100 mm. The undecylic acid of Krafft[1] boils at 212.6° at 100 mm., and its melting point is 28.5°, but apparently it does not distil at ordinary pressure without decomposition. Other data for comparison are wanting. The results of this investigation are the more remarkable inasmuch as they are not in accordance with the general theory that the natural fats

[1] Berichte der deutschen chemischen Gesellschaft, **11**, 2219; **12**, 1667.

contain only acids with an even number of carbon atoms in the molecule, although the occurrence of inactive valerianic acid in dolphin oil[1] would be at least one exception to that rule, and others have been noticed, which demand further confirmation, however. Until some causal connection between the occurrence in natural fats and the even number of carbon atoms has been established, too much reliance should not be placed on the general rule.

If opportunity offers we shall endeavor, during the next university year, to resume the study of this interesting acid and its derivatives.

Laboratory of the University of California, BERKELEY, *May* 10, 1882.

Contributions from the Chemical Laboratory of Rutgers College.

VI.—ON THE PRECIPITATION OF TITANIC ACID.

By PETER T. AUSTEN AND F. A. WILBER.

In the analysis of titaniferous ores by fusion with the carbonates and nitrates of the alkalies, the fused mass is soaked out with water, the solution acidified with chlorhydric acid, evaporated to dryness to render the silica insoluble, then taken up with chlorhydric acid and water, and filtered. In the residue consisting of silica, containing more or less ferric oxide, titanic acid and phosphoric acid, the silicic acid is determined by expulsion with fluohydric acid. The residue consisting of titanic acid, ferric oxide and phosphoric acid is then fused with an alkaline bisulphate and the resulting solution added to the chlorhydric acid solution, which has been freed from platinum by treatment with hydrogen sulphide.

To determine the titanic acid in this chlorhydric acid solution it is necessary to precipitate an aliquot part of it with an excess of potassium hydrate (first oxidizing the ferrous salts by potassium chlorate), filter off and wash the bulky gelatinous precipitate of ferric oxide, titanic acid, phosphates, etc., dissolve the mass in sulphuric acid, reduce and precipitate the titanic acid by boiling. It is not practicable to precipitate the titanic acid directly by boiling the chlorhydric acid solution, since the precipitation by this method is not complete, and when thus precipitated it runs through the filter-paper as soon as the wash-water ceases to be acid. If the wash-water is acidified with chlorhydric acid, the precipitate is more or less dissolved.[1] The filtration and washing of this precipitate is extremely irksome, and, like that of the basic acetates, is seldom really perfect.

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[1] Chevreul, cited in Roscoe and Schorlemmer's Chemistry, **3**, I, 618.

On the other hand the method of decomposing the ores with an alkaline bisulphate, which yields at once a sulphuric acid solution, is often very tedious, on account of the stability of many ores toward this flux and the length of time that it frequently takes to remove the fused mass from the crucible, especially when potassium bisulphate has been used and the temperature has been too high, or not enough sulphuric acid has been added at the close. There are but few ores which are not decomposed by the alkaline carbonates and nitrates when the fusion is finished in a small Fletcher injection furnace, and if rightly handled during cooling the fusion will come out of the crucible in a few hours.

The results obtained by Streit and Franz[2] do not seem to have been utilized in the analysis of titaniferous iron ores. According to these authors, titanic acid may be precipitated from its chlorhydric acid solution in a form which can be easily filtered and washed, when to the solution one-third of its volume of sulphuric acid (containing one-sixth volume of H_2SO_4) and one-fifth of its volume of acetic acid are added. In using this method, however, we have found that when considerable amounts of chlorhydric acid were present, the addition of so much sulphuric acid prevented the precipitation of the titanic acid.

If also it is the intention to determine manganese by the beautiful oxalate method of Classen[3] which does away with the tedious basic acetate procedure, it is of importance that but a small amount of sulphates should be present.[4] We were led, therefore, to experiment on the precipitation of titanic acid from its chlorhydric acid solution by the addition of acetic acid alone, and find that it answers the purpose in every way as well, if not better, than when a mixture of acetic and sulphuric acids is employed. The titanic acid is precipitated from its reduced solution on boiling as a flocculent precipitate which settles rapidly and well. The hot solution can be easily filtered without waiting for it to settle. The precipitate shows no tendency to run through the paper if washed with hot water acidified with acetic acid. In fact the addition of a little acetic acid to the wash-water, in cases where the titanic acid, precipitated by the usual method, shows a tendency to run through, stops it at once. The titanic acid when precipitated in the presence of acetic acid, from a chlorhydric solution containing ferrous salts of iron, is as free from iron as when precipitated by the usual method. It is rare that a precipitate of titanic acid is obtained perfectly free from iron in actual analysis when the solution contains a considerable amount of iron. In the presence of phosphates it always contains iron and phosphoric acid,[1] and has to be worked over again.

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[1] Rose, Quant. Anal. 1871, **2**, 313.

[2] J. pr. Chem. **108**, 65.

[3] Fres. Zeit. **18**, 175.

[4] Fres. Zeit. **18**, 186.

A number of experiments were made with titaniferous ores to ascertain if the precipitation of titanic acid from a chlorhydric solution in the presence of acetic acid was complete. In no case could the slightest trace of titanic acid be detected in the filtrates by means of tin and chlorhydric acid.

There are, of course, many modifications possible in the analysis of titaniferous ores, and various applications can be made of this method of precipitating titanium, but the following course seems to offer some advantages.

The ore is fused with alkaline carbonates and nitrates, and after taking up with water in the usual manner, is acidified with chlorhydric acid and evaporated to dryness to render the silica insoluble. It is then moistened with chlorhydric acid and treated with a little warm water till solution of the soluble parts has been effected, after which it is allowed to cool, and then diluted, without filtering, to 400–500 cc. Sulphurous acid is next added, and then 50–60 cc. of acetic acid. On boiling in the usual manner, the titanic acid will be precipitated in a flocculent and easily filterable state. The whole is then filtered and washed with hot water containing a little acetic acid. If the ore does not contain phosphoric acid this precipitate will be quite free from iron, and after expelling the silica by treatment with ammonium fluoride and sulphuric acid is generally pure enough to be taken as titanic acid, although in cer-

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[5] Bogardus, Am. J. Sci. **3**, 8, 334.

tain cases where the amount of titanic acid is small and the amount of iron large, a re-fusion is often necessary. In case the ore contains phosphates, the titanic acid precipitate will always contain iron and phosphoric acid. In this case, the residue, after expelling the silica with ammonium fluoride, can be fused with sodium carbonate and the fusion extracted with water, which dissolves the sodium phosphate and leaves the sodium titanate and ferric oxides.[1] This residue is then fused with a little sodium bisulphate, and the titanic acid precipitated after reduction by boiling. The filtrate containing the iron which was precipitated with the silica is now added to the filtrate from the original precipitation of the titanic acid, and the acidified filtrate from the fusion of the titanic acid with sodium carbonate,[2] and the united solutions analyzed for alumina, iron, manganese, calcium and magnesia, after freeing it from platinum by precipitation with hydrogen sulphide.

NEW BRUNSWICK, N. J.

REVIEWS AND REPORTS.

REPORT ON PROGRESS IN PHYSIOLOGICAL CHEMISTRY.

[*Continued from Vol.* 3, 450.]

GASTRIC DIGESTION AND THE PRODUCTS FORMED.

Digestion in the Stomach and Intestines.—Nearly all our knowledge in regard to the chemistry of the digestive process is based upon experiments on artificial digestions carried on outside the animal body. Recently, however, Schmidt-Mülheim[3] under the guidance of C. Ludwig, of Leipzig, has undertaken a methodical examination of the alterations which proteid bodies undergo in the alimentary canal, studying for this purpose the normal process as carried on in the digestive apparatus of dogs. The animals employed were as nearly alike as possible in weight, race and temperament, and prior to the experiment were kept for two days entirely without food, in order to have the digestive apparatus freed as far as possible from all traces of previous food. The proteid material employed was horse-flesh, which, after being freed from fat and collagenous tissue, was finely divided and boiled with water for fifteen minutes for the complete removal of all crystalline constituents such as creatin, etc. The content of albumin in the so prepared food was calculated from a determination of nitrogen made according to the method of Dumas.

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[1] Drown and Shimer, this Journal, **4**, 6.
[2] This is hardly necessary unless phosphoric acid is to be determined in this solution.
[3] Du Bois Reymond's Archiv. f. Physiolog. 1879, 39.

In carrying out the experiments each dog received 200 grams of flesh, and after the lapse of a definite time the animal was killed by the injection of potassium cyanide into the thorax. The abdomen was then immediately opened and the contents of the stomach and intestines were separated by two ligatures placed at the commencement of the duodenum. The contents of the two were then removed separately, and the walls of the canal were freed from any adhering matter by thorough washing with water. The undigested portion was collected by filtration, and after thorough washing with water was dried, and from a determination of its nitrogen the quantity of undissolved albumin was calculated.

In order to determine the dissolved albumin a measured quantity of the filtered fluid was mixed with ferrous acetate and a small quantity of ferrous sulphate, and then boiled. The brown flocculent precipitate was then carefully collected, washed and dried at 100° C. Its content of nitrogen was determined by the method of Dumas, and from the data so obtained the amount of soluble albumin was calculated; 15.6 per cent. being considered the average amount of nitrogen present in albumin. To separate the peptones the united filtrate and wash-water from the albumin precipitate were concentrated to a small bulk, and when cold the fluid was made strongly acid with acetic acid, and then phosphotungstic acid was added until a filtered portion of the solution failed to give even the faintest red color with cupric sulphate and sodium hydroxide. The white tungstic acid precipitate was treated in the same manner as the iron precipitate, and from the content of nitrogen the amount of peptones was calculated, using the same factor as before. The crystalline decomposition products were looked for in the albumin and peptone free solution from the intestines. The method consisted in evaporating the filtrates to dryness and dividing the residue into three portions: for the leucin one portion was extracted with hot alcohol, and in this concentrated extract the easily identified crystals of leucin were sought for; for the detection of tyrosin another portion of the residue was examined by Piria's method; finally, in the third portion of the residue nitrogen was determined, from which the total amount of crystalline decomposition products of the albumin was calculated; in this latter case, however, the results are undoubtedly too high, from the presence of portions of nitrogenous constituents of bile. Following are the results obtained in five experiments:

	1 hour after feeding.	4 hours after feeding.	6 hours after feeding.	9 hours after feeding.	12 hours after feeding.
Soluble albumin in stomach,	2.262 grams	2.086 grams	2.096 grams	1.810 grams	0.049 grams
Peptone in stomach,	3.087 “	3.312 “	2.912 “	3.422 “	0.083 “
Unaltered food in stomach,	50.389 “	25.928 “	17.833 “	7.077 “	0.120 “
Dissolved albumin in intestines,	0.482 “	0.436 “	0.917 “	0.438 “	0.202 “
Peptones in intestines,	0.512 “	0.498 “	1.352 “	1.222 “	0.820 “
Undissolved matter in intestines,	1.914 “	1.912 “	2.743 “	1.840 “	1.936 “
	58.746 “	34.622 “	27.853 “	15.329 “	3.210 “
Albumin fed,	61.150 “	65.817 “	64.000 “	62.013 “	61.705 “
Albumin absorbed,	2.404 “	31.195 “	36.147 “	46.684 “	58.515 “

Leucin and tyrosin were found only in the merest traces.

From these results it is clearly seen that a much longer time is needed for the completion of the digestive process than has hitherto been supposed. Even after nine hours' digestion, unaltered food is still found in the stomach, and food too which from its finely divided condition and by boiling has been changed to the easiest state of digestibility possible. Only after twelve hours can the digestion be considered as finished. The following table clearly shows several other points connected with digestion in the stomach which are worthy of notice.

Time after feeding,	Proportion of dissolved albumin to peptones.	Quantity of dissolved albumin and peptones.	Weight of peptones.
1 hour	1 : 1.4	5.349 grams	3.087 grams
2 hours	1 : 2.0	5.448 “	3.653 “
4 “	1 : 1.6	5.398 “	3.312 “
6 “	1 : 1.4	5.008 “	2.912 “
9 “	1 : 1.8	5.052 “	3.242 “
12 “	1 : 1.8	... “	... “

It is thus very apparent that among the products formed in gastric digestion, the peptones at all times in the process exceed in amount the dissolved albumin; also that the relative proportion of these two proteids is not materially altered in the different stages of digestion. Again, it is to be noticed that the total quantity of dissolved albumin and peptones present in the stomach is practically the same at all times during the digestion, and also that the quantity of peptones varies only slightly. These facts would seem to indicate that after the formation of a definite quantity of the digestive products, the transportation of these bodies keeps pace with the digestion, so that at no time can there be an accumulation of the digestive products. Mülheim is of the opinion, from the composition of the contents of the intestinal canal, that a not inconsiderable portion of the soluble contents of the stomach passes on into the intestines, instead of being at once absorbed from the stomach.

In the intestinal digestion Mülheim found in all his experiments that the contents of the small intestines possessed an acid reaction; this was the case not only with the fluid contents of the upper end of the small intestines, but also with the brown and more solid mass at the lower end. This result, which is contradictory to the prevalent idea that the three alkaline digestive fluids, bile, pancreatic and intestinal juices, are sufficiently strong to render the entire contents of the intestinal canal at once alkaline, has an important bearing on pancreatic digestion. While in alkaline digestive fluids putrefaction soon shows itself with simultaneous formation of crystalline decomposition products together with large quantities of indol, the digestion of albumin by an acid pancreatic juice is more analogous to a pure digestive process. Again, Mülheim remarks that the acid reaction is a necessity for the formation of the viscous yellow precipitate which is found in the small intestines; which precipitate Mülheim is inclined to think is of great importance to pepsin digestion. Calling attention to Brücke's statement that pepsin possesses the property in the highest degree of attaching itself to small particles, he reasons that the bile precipitate serves the purpose of holding temporarily the pepsin, so as to prevent the destruction of the trypsin, which according to Kühne is digested by pepsin in acid solution, the ferment being liberated again when the bile precipitate is dissolved in consequence of the ultimate alkaline reaction, which usually appears at the end of the small intestines. Thus it is the rôle of the precipitate to prevent the destruction of the pancreatic ferment by the gastric juice in the small intestines. Further on, where the fluids are alkaline, the pepsin is powerless, being inactive in an alkaline medium.

Again, the amounts of crystalline proteid decomposition products found in the intestinal canal under the physiological conditions described, are so unimportant it would appear that only an inappreciable quantity of albumin is absorbed in the form of crystalline products in normal digestion.

Absorption of Albumin in the Stomach.—Relative to the absorption of albumin in the stomach, Dr. v. Anrep[1] has experimented with dogs, introducing into the stomach by means of a stomach fistula a definite amount of syntonin in solution. The pyloric opening of the duodenum was closed, and prior to the experiment the animal was deprived of food for 24 hours, while just before the albumin solution was introduced the stomach was thoroughly rinsed with water. The solution of albumin was introduced into the stomach by the fistula, which was then stoppered. After a definite time the contents of the stomach were emptied into a dish, and in the fluid the amounts of syntonin and peptones were determined by analysis. The following table shows the results:

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[1] Die Aufsaugung im Magen des Hundes. Du Bois Reymond's Archiv. 1881, 504.

Am't of substance introduced.	Am't found in stomach.		Quantity absorbed.	Per cent. of absorbed albumin.	Length of time.
	Syntonin.	Peptone.			
4.2 grams syntonin,	0.327 gram	2.898 grams	0.975 gram	23.3 per cent.	1 hr. 30 min.
12.79 " "	6.534 "	2.688 "	3.537 "	27.9 "	1 " 40 "
2.124[1] " "	0	0.729 "	1.397 "	65.6 "	1 " 40 "
5.91 " peptone,	..	3.099 "	1.872 "	31.7 "	1 " 45 "
12.25 " "	..	8.103 "	4.847 "	33.9 "	1 " 45 "

It would thus appear from Dr. v. Anrep's experiments that the stomach possesses the power of absorbing peptones, though as to the relative absorption by the stomach and intestines little is shown.

Decomposition of neutral Fats in the living Stomach.—Dr. Ogata,[2] by the use of methods similar to those employed by Dr. v. Anrep, has studied the behavior of neutral fats in the living stomach of dogs. Prior to the experiment the stomach of the fasting animal was thorough rinsed, through the fistula, with .5 per cent. salt solution; 50-60 cc. of perfectly neutral olein were then introduced into the stomach, remaining there from two and a half to three hours. At the end of this time Dr. Ogata succeeded in four cases in finding clear evidence of the presence of oleic acid.

R. H. CHITTENDEN.

(*To be continued.*)

RECENT PROGRESS IN AGRICULTURAL SCIENCE.

[*Continued from p.* 152.]

In regard to the sources of *nitrogen* to the plant, little that is new has been reported. Ad. Mayer[3] has reinvestigated the question of the assimilability of ammonia by the leaves of plants. He finds that the higher plants are capable of taking up ammonium carbonate through their leaves, both when it is dissolved in water and when it is in the gaseous state; and that the process is not simply a mechanical one, but that the nitrogen thus introduced into the plant is assimilated. Too great concentration of the ammonium carbonate is fatal to the life of the plant, but small amounts were found to be harmless and to exert no effect on the respiration of the plant. In view of the fact that leguminous plants are popularly believed to gather considerable quantities of nitrogen from the air, trials were made with these plants, but they were not found to have any peculiar power in this respect. As to the practical significance of this capacity of vegetation to assimilate nitrogen through its leaves, Mayer comes to the conclusion that it is very small.

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[1] This experiment yields too high results, owing to an incomplete washing out of the stomach.

[2] Du Bois Reymond's Archiv. 1881, 515.

[3] Jahresber. agr. Chem. 16-17 **1**, 286.

Experiments by Hässelbarth[1] and Wein,[2] on the relative value of nitrates and ammonia as plant food, gave the same results as most previous experiments on this subject, viz. that, while nitrates are readily assimilated, ammonia is taken up with difficulty, if at all. Hässelbarth experimented on barley, growing it in purified quartz sand watered with solutions of plant food. The normal solution contained

2	mg. equivalents	KH_2PO_4
1 "	"	KCl
1.6 "	"	$MgSO_4$
5 "	"	$Fe_2(HO)_6$
16 "	"	$Ca(NO_3)_2$

The ferric hydrate was mixed with the sand and the remaining substances given in solution. In four other experiments the same amount of nitrogen was supplied respectively as ammonium sulphate, phosphate [$NH_4H_2PO_4$], chloride and nitrate, while the calcium was supplied as sulphate. In a second series of experiments the same mixtures were used, but with the addition of 40 grams of $CaCO_3$ to each pot, while a third series was added precisely like the second, except that no plants were introduced, the pots serving to test the amount of nitrification taking place. At the close of the experiments the total dry matter, nitrogen, and lime of the plants (exclusive of roots) were determined. It was found that nearly the total amount of nitrogen present as nitrates was assimilated, as was also that of the ammonium sulphate and chloride *in the presence of* $CaCO_3$. In those cases in which no $CaCO_3$ was present, only about half the nitrogen of the last named salts was assimilated, and only about one-third as much dry matter was produced as in the other cases. The ammonium phosphate seemed to be the least adapted to the barley plant of any of the salts tried, only about three-fifths of its nitrogen being assimilated in the presence of $CaCO_3$, and only about one-seventh in its absence, while the amount of dry matter in the latter case was even less than that produced when no nitrogen whatever was added to the soil. Hässelbarth believes that the better results obtained in the presence of $CaCO_3$ are due to the nitrification of the ammonium salts, favored by the presence of the calcium carbonate, and in fact in his control pots from 36 to 52 per cent. of the nitrogen was converted from ammonia to nitric acid during the time of the experiments. Another explanation of the favorable action of $CaCO_3$ is, however, possible. It is a well-established fact that, when salts of ammonium are offered to the roots of a growing plant, the base is taken up more rapidly than the acid, thus leaving the solution acid, and that if the process continues the acidity may soon become such as to injure or destroy the plant. Hässelbarth makes no mention of any precautions having been taken to prevent this action in his experiments, and it is quite conceivable that the $CaCO_3$ was of benefit simply by neutralizing the acid set free from the ammonium salts and thus preventing it from injuring the plant. This is perhaps also indicated by the fact that the plants in the pots containing $CaCO_3$ assimilated more lime than any of the others, even those fed with calcium nitrate. If the action of the calcium carbonate was such as we have supposed, it is evident that the plants had presented to them an extra quantity of soluble lime salts, some of which would probably be taken up. While, then, it is probable that nitrification explains part at least of the good effects of the $CaCO_3$ in these experiments, the results are not conclusive against an assimilation of ammonia.

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[1] Landw. Versuchs-Stationen, **21**, 363.

[2] Jahresber. agr. Chem. N. F. **2**, 190.

Wein's experiments were very similar to those of Hässelbarth, except that he used artificial humus instead of sand, and cultivated several kinds of plants, including oats, peas and soja beans. His results appear to have also been much the same, but in the experiments with ammonium sulphate a renewed growth was noticed toward the end of the experiment, as in Beyer's well-known experiment, and apparently from the same cause, viz. nitrification of the ammonia.

Wein's experiments were suggested by the previous experiments of Lehmann[1] on the same subject, and Hässelbarth's results are of interest in the same connection. Lehmann's most striking results were obtained with maize by the method of water culture. On attempting to grow young maize plants in solutions identical as regards mineral matters, but furnishing nitrogen respectively as calcium nitrate and ammonium sulphate, the plants of the ammonia series grew luxuriantly at first, while those of the nitric acid series showed all the signs of deficient nutrition. After about forty-one days, however, a sudden change was observed. The plants of the nitric acid series became of a healthy green, and from this time on grew rapidly and normally, while the plants of the ammonia series, on the other hand, lost their healthy color, became sickly, and remained so during the rest of the experiment, falling much below the nitric acid plants in the amount of crop.

On removing sickly plants of the ammonia series into solutions containing nitrates they promptly recovered and grew normally, while healthy plants of the nitric acid series, when removed into solutions containing only ammoniacal nitrogen, speedily took on the sickly character of the plants raised in such solutions. In the same way, in the earlier stages of the experiment, the sickly plants of the nitric acid series recovered within two days when placed in the ammonia solution, while the ammonia plants became sickly when placed in the nitrate solution.

Similar, but not quite so decided, results were obtained with tobacco plants cultivated in sand.

Lehmann concludes that these two plants in their early stages of growth require their nitrogen to be presented in the form of ammonia, while in later stages of development they can assimilate it only from nitrates. Buckwheat and yellow lupines, on the contrary, he found to require nitrates throughout their whole period of growth.

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[1] Biedermann's Central-Blatt. Jahrg. **4**, 403.

If we accept Lehmann's results as correct, then Hässelbarth's and Wein's experiments indicate that the plants which they experimented upon belong to the class of "nitric acid plants," *i. e.* plants which require nitrates throughout their growth; and in manuring them we should either use fertilizers containing nitrates or apply our nitrogenous fertilizers sufficiently long beforehand to permit their nitrification in the soil to begin at least.

Lehmann's results, or rather the conclusions which he draws from them, seem, however, to be somewhat questionable. Hampe,[1] in 1867, produced a maize plant 2½ feet high, bearing 40 seeds, in a solution intended and asserted to contain no nitrates. At a certain stage of growth the plants showed signs of disturbed nutrition, but recovered in a week or two. Hampe's conclusion is that "the plants, while young, were unable to assimilate ammonia or did so with difficulty, but acquired the power with a certain age." Wagner,[2] in 1868, obtained exactly the same results as Hampe. These results appear to be directly opposed to Lehmann's, but still, in view of the readiness with which, as we now know, ammonium salts are nitrified in dilute solutions, too much weight is not to be attached to them. It is possible that the renewed growth in Hampe's experiments was due to the formation of nitrates in the solution.

A more weighty argument against Lehmann's theory is the fact that luxuriant maize plants have been raised in solutions containing from the start no nitrogen except in the form of nitrates. Knop,[3] for example, produced a maize plant having a dry weight of over 50 grams, or a green weight of 330 grams, and bearing an ear containing 140 ripe seeds, in a solution containing the nitrates of potassium and calcium as sole sources of nitrogen. Knop also recommends a solution containing nitrate and phosphate of potassium, nitrate of calcium, sulphate of magnesium, and a little phosphate of iron, as well adapted to water-culture experiments, although he does not mention maize in particular; and in the very numerous experiments with other plants which have been made, nitrates have invariably proved a sufficient source of nitrogen. While, then, it would hardly be safe to reject Lehmann's results, they certainly require confirmation before they are accepted.

The most noticeable recent experiments on the sources of the *ash ingredients* of plants are those of Grandeau,[4] on the functions of the so-called *matière noir* of fertile soils, by which term he designates the black organic matter, insoluble in water or acids, but soluble in alkalies, which can be extracted from the soil by ammonia. We have already seen that the organic matter of the soil does not, in all probability, contribute directly to the growth of the plant to any appreciable extent. Notwithstanding this, however, it is a well-known fact that in general those soils which are distinguished for their fertility contain much humus, and that the addition of organic matter to soils deficient in it usually improves them. In Grandeau's opinion, the effect of the organic matter on the physical character of the soil is not a sufficient explanation of its action, and his hypothesis in regard to the rôle of the *matière noir*, the result of much study and experiment, attributes its chief value to a peculiar chemical action between it and the inorganic matters of the soil. While not denying that the roots of plants may extract nourishment from the solid particles of the soil, he holds that no *agriculturally profitable* production can take place unless some substance is present in the soil which can dissolve the comparatively insoluble mineral food which it contains and present it to the plant in a more assimilable form. To do this is the office of his *matière noir.* It is not itself assimilated by plants, but it unites with the inorganic plant food present in the soil to form a peculiar compound, from which the plant takes the potash, phosphoric acid, etc., which it needs, leaving the organic residue to take up a fresh portion of these substances from the soil. That is, the *matière noir* serves as a carrier of plant food between the soil and the plant, in a manner analogous to the action of the oxides of nitrogen in the manufacture of sulphuric acid. To extract this *matière noir* from the soil, Grandeau proceeds as follows: The soil is first treated with very dilute hydrochloric acid to decompose the insoluble lime compound in which the *matière noir* exists in the soil. The acid is washed out with water, and on then treating the soil with ammonia, a solution of the *matière noir* is obtained, which, on evaporation, deposits the substance as a shining, carbonaceous mass. The substance thus obtained contains, besides organic matter, a greater or less amount of ash, composed to a considerable extent of silica, but containing also all the mineral nutrients of the plant, the predominant ingredients, after silica, being the phosphates of iron and alumina. Analyses of the ash of *matière noir* have been made by Grandeau, and also by Pitsch. Grandeau's results were:

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[1] Johnson "How Crops Feed," 303.
[2] *Ibid.* 304.
[3] Kreislauf des Stoffs, 2, 239.
[4] Annales de la Station Agronomique de l'Est, 1878, 225–352.

Silica,	35.60
Oxide of iron (combined with silica),	18.36
Oxide of manganese (combined with silica),	0.18
Lime (combined with silica),	3.55
Tribasic phosphate of lime,	2.66
Phosphate of iron,	34.41
Magnesia,	1.28
Potash,	3.94
	99.98

Pitsch obtained the following figures:

	Clay Soil.	Sandy Soil.
Chlorine,	0.07	trace
Char.	6.00	0.08
Silica,	33.70	17.19
Iron oxide,	17.03	24.39
Alumina,	3.40	5.50
Phosphoric acid,	29.94	38.10
Manganese,	1.04	5.73
Lime,	2.35	1.68
Magnesia,	3.53	1.64
Potash,	7.30	4.06
Soda,	3.08	0.13
Sulphuric acid,	trace	0.16
	107.44	98.66

In the ammoniacal solution of the *matière noir*, according to Grandeau, the mineral matters cannot be detected by the ordinary reagents, and he therefore assumes the existence of a peculiar chemical compound between them and the organic matter, which is the means of supplying the plant with its ash ingredients in the manner described. The facts on which Grandeau bases his hypothesis are substantially the following:

1st. In a large number of soils examined by him, the actual fertility, as shown by experience, was found to correspond quite closely with the amount of *matière noir* extracted from them by ammonia, and still more closely with the amount of ash ingredients contained in the latter, while neither the total organic matter nor the amount of mineral matter extractable by acids showed such a relation.

2d. On subjecting a solution of *matière noir* to dialysis, the mineral matters passed readily through the membrane while the organic matter remained behind. Since the solution contained all the essential ash ingredients, its capacity to nourish plants was thus shown. Plants were also grown successfully in sterile sand watered with a solution of *matière noir*. At the close of the experiment the roots were found covered with black, flocculent organic matter containing very little ash. No trace of the organic matter having entered the roots could be perceived. The solution, which was at first alkaline, assumed an acid reaction in the pots and became decolorized.

3d. To show the necessity of the *matière noir* for the growth of plants, a kilogramme of Russian "black earth" was halved. From one-half the *matière noir* was extracted, while the other half was left in its natural state, and in each half a bean plant was grown. That in the original soil grew normally, while that in the extracted soil grew very feebly and produced only a few early withering leaves.

Experiments were also made as follows: Four boxes of soil, having one square meter of surface each, which had been treated exactly alike in two successive vegetation experiments, were used. Two of them contained a calcareous soil, the other two a clay soil. From one box of each pair the soil was removed to the depth of 20 cm., mixed with an equal weight of a sterile peat, and the mixture replaced in the box. On the next day the soil of the other two boxes was cultivated to the depth of 20 cm., and all four boxes were manured with 100 grams of dicalcic phosphate. Eleven days afterward the soil was again cultivated and 30 grams of chevallier barley sown in each box. The crop of grain in each box was:

I. Calcareous soil without peat, 430 grams.
II. “ “ with “ 800 “
III. Clay “ without “ 600 “
IV. “ “ with “ 775 “

To show that these differences were really due to the *matière noir*, Grandeau gives the following table:

	100 grams soil contained of *matière noir*.	The *matière noir* of 100 grams soil contained of P_2O_5.	Crop.
Box I.	0.98 gram.	0.03 gram.	430 grams.
“ II.	1.14 “	0.10 “	800 “
“ III.	1.20 “	0.06 “	600 “
“ IV.	2.22 “	0.08 “	775 “

The favorable action of the peat continued to show itself through several subsequent years, and imparted to the soils superior physical properties.

In considering Grandeau's theory of the rôle of the organic matter of the soil, two distinct questions present themselves: first, does the amount of plant food extracted from a soil by dilute ammonia furnish an appropriate indication of its fertility; and second, if this is the case, are Grandeau's views as to the manner in which the humus of the soil contributes to the nutrition of plants correct? The answer to the first of these questions is to be found by the statistical method; by the examination of a large number of soils whose crop-producing power is known. Such examinations have been made by Grandeau himself on thirty soils, by Pitsch[1] on fifteen soils, and by Tuxen[2] on five soils.

Grandeau determined the total amount of organic matter in his soils, the amount of organic matter soluble in dilute ammonia after treatment with dilute acid, and in the latter the total ash and the phosphoric acid, the latter ingredient being regarded as one of the most important. It was found that the fertility of these soils was in general proportional to the amount of *matière noir* which they contained, and more closely proportional to the amount of phosphoric acid which the latter contained. The fifteen soils examined by Pitsch also gave the same result.

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[1] Landw. Versuchs-Stationen, **26**, 1.

[2] *Ibid.* **26**, 114.

Tuxen experimented on a sample of soil from the Nile valley, a sample of leaf mould, and three samples of a clay soil from near Copenhagen. The last three samples were of the same soil, but had received different treatment, one not having been manured for 21 years, one having received only mineral fertilizers for 17 years, and the third having been heavily manured with stable manure for 17 years.

The Nile soil, in spite of its great fertility, stood next to the last as regards the amount of phosphoric acid extracted. The other soils stood about in the order of their fertility in this respect, but the differences were comparatively small, and in Tuxen's opinion too small to account for the differences in fertility. The amount of ash ingredients extracted by the preliminary treatment with dilute acid seemed to correspond more closely with the actual fertility.

In three of the samples examined by Pitsch, the preliminary treatment with dilute acid also removed a large proportion of the phosphoric acid, so that very little was left for the ammonia to remove. In these cases Pitsch adds the P_2O_5 extracted by dilute acid to that found in the *matière noir*, and thus brings his results into harmony with Grandeau's. If we pursue the same course with Tuxen's soils, the results agree better with the observed fertility, though the two are by no means numerically proportional.

On the whole it would appear from the experiments thus far made that the amount of mineral matters, particularly of phosphoric acid, extracted from a soil by ammonia after previous treatment with dilute acid, may aid essentially in forming a judgment as to its fertility. It will be noticed that the most unfavorable results were obtained on clay soils.

Admitting, now, that the determination of the matters extracted by ammonia affords an approximate measure of the fertility of a soil, are Grandeau's views as to the peculiar functions of the *matière noir* correct? That the humus of the soil is *useful* is denied by no one, but is it *essential?*

In the first place it is to be remarked that the *matière noir* exists in the soil in an *insoluble* form; a fact admitted by Grandeau, since he employs a preliminary treatment with dilute acid, as he expressly states, to set it free from its insoluble lime and magnesia compounds.

This fact, however, deprives all Grandeau's experiments on the diffusibility of the ash ingredients of his *matière noir* and on the nutrition of plants by means of a solution of it, and all his theories as to its action in presenting plant food to the roots of the plant in a soluble form, of all value in this regard. If the *matière noir* exists in an insoluble compound in the soil, it may furnish food to the plant, but it does not present it in a soluble form, unless indeed we are to suppose that the roots first excrete an acid and then an alkali.

It is of course conceivable, however, that the *matière noir*, although insoluble, may still be an important source of plant food, since it is well known that the roots of plants exert a considerable solvent action on the ingredients of the soil.

What, then, are the proofs which Grandeau brings forward of the existence of a peculiar compound of organic and inorganic matter which is the only source from which agricultural plants can derive food in sufficient quantity to render their cultivation profitable?

First he calls attention to the properties of the matter extracted from the soil by ammonia after treatment with dilute acid. The dark brown or black solution thus obtained contains large amounts of the phosphates and silicates of iron, aluminum and calcium, compounds which are not soluble in water or ammonia. Moreover, the ash ingredients of the solution cannot be detected by the ordinary reagents. In regard to this it may be said in the first place that the solution is not simply a solution of ammonia, but of humate of ammonium (using the term humate in a general sense), and it is well known that the presence of organic matter and of ammonium salts may have a very decided solvent action, and may prevent the precipitation of other substances without necessitating the assumption of a chemical union. Furthermore, Pitsch (*loc. cit.* 38) has found that humate of ammonium dissolves phosphates of calcium and iron, acting in this respect like ammonium citrate, and that from the solution so obtained the phosphoric acid can be precipitated by magnesia mixture if a large excess of the latter be used, just as is the case with the ammonium citrate solution. Moreover, in his diffusion experiments Grandeau found that the mineral matters of the *matière noir* passed through the membrane into the water outside it, where, so far as can be judged by the account given, they remained dissolved. If these mineral matters could thus remain dissolved in water containing, according to Grandeau, no trace of organic matter, it seems hardly necessary to assume that they were previously combined with the organic matter in order to explain their solubility in a solution of humate of ammonium.

It was hardly to be expected that a solution of ammonia should not remove some mineral matters from the soil. The preliminary treatment with acids must set free more or less silica from the hydrous silicates of the soil, which would then dissolve in the ammonia; though Grandeau makes the somewhat remarkable statement that the ammonia does not attack the silica of the soil, and gives this as one of his reasons for preferring it to a fixed alkali. The humate of ammonium, as we have seen, acts as a solvent of the more finely divided portions of the phosphates of the soil, while the presence of potash, soda, etc., in the extract is easily accounted for by an exchange of bases with the hydrous silicates just as in other cases of soil absorption. That the quantity of mineral matter thus extracted should furnish a better indication of the fertility of the soil than the amount extracted by strong mineral acids might have been safely prophesied beforehand, but the facts afford no proof of the existence of any peculiar compound in the soil.

Attention has already been called to the fact that clay soils have shown the least agreement with the theory. Now these are exactly the soils which contain the largest proportion of hydrous silicates and insoluble phosphates, and show the greatest absorptive power. That is, they usually contain comparatively large amounts of plant food in a form insoluble in water, but, as we have reason to believe, readily attacked by the roots of plants, and also readily dissolved by dilute acids, but in combinations from which it would not be likely to be extracted very freely by ammonia or humate of ammonium. It is thus quite natural that the preliminary treatment with acid should rob these soils of a considerable portion of their available plant food, as in Pitsch's experiments, and that the amount extracted by ammonia should not measure as accurately the amount of available matters as in the case of a sandy soil, for example.

Grandeau also brings forward in support of his views the vegetation experiments with the Russian "black earth" in its natural state and deprived of its *matière noir*, and with soils to which organic matter had been added which have already been described. In the first of these experiments he claims that the fact that the bean refused to grow in the extracted soil is proof that the *matière noir* is indispensable. This, however, is begging the question. What the experiment really shows is that the treatment with acid and alkali removed almost all the available plant food. Whether all or any of it existed in the soil in combination with the organic matter, or whether if the latter alone could have been removed the fertility of the soil would have been affected, the experiment does not show.

Equally defective are the conclusions drawn from the experiments in which sterile peat was added to two soils, in that its effect on the physical properties of the soils is ignored. That peat is a useful amendment on many soils has long been known; that along with its physical effects it acts to increase the supply of available plant food is also true; but while Grandeau's results do not negative his theory, neither do they sustain it.

In short, Grandeau's experiments do not prove his theory, because they admit of other and, as it seems to the writer, simpler and more probable explanations.

The belief of practical agriculturists in the value of organic matter in the soil needs no such theory to reconcile it with the well established fact that the food of vegetation is mineral matter.

We divide the total plant food in the soil into two portions; one, and a comparatively small one, exists either actually in solution or in a comparatively soluble form, and is the active portion of the soil; the other, and by far the larger, portion is simply rock fragments of various sizes, and is not immediately available to the plant. Every little fragment, however, is constantly subject to the same "weathering" which goes on in the larger masses, and under the influence of changes of temperature, frost, and the solvent action of water and saline solutions, is gradually rendered available to the plant. If by any means the amount of organic matter in the soil be increased, as in Grandeau's experiments for example, especially if it be finely divided and uniformly distributed, we have, as experiment has shown, a considerable increase in the carbonic acid of the soil, and hence an increase in the rapidity of the solvent action which converts rock dust into available plant food. Add to this the solvent action of the acids formed by the decay of organic matter, and the effect on the porosity, temperature, permeability, etc., of the soil, each in its turn reacting on the rate of weathering as well as on the growth of the crop, and we can readily see why "humus" should have a high value in the soil. We can see why a soil like the Russian black earth, where every mineral particle has its adjacent organic particle continually furnishing matter to dissolve it, should be a much more abundant source of plant food than a soil equally rich in minerals but lacking the organic matter.

Finally, the natural organic matter of the soil is a consequence as well as a cause of fertility. A large amount of humus in a soil implies an abundant previous growth of vegetation, and this in its turn implies a soil of at least moderate original fertility.

It is Grandeau's merit to have called attention emphatically to the value of the organic matter of the soil, and to have brought students of agricultural science to recollect, what they knew before, that the mineral matters of the soil are not the sole elements that determine its agricultural value; but his theory of the peculiar nature and functions of the *matière noir* seems to be one of those exaggerations into which it seems to be a law of nature that every one shall fall who sees clearly and presents forcibly and effectively any single aspect of a subject.

H. P. Armsby.

The Manufacture of Steel and Ingot Iron from Phosphoric Pig Iron.

A paper on this subject, by Sidney G. Thomas and Percy C. Gilchrist, was recently read before the Society of Arts, London. As it contains some new and interesting information in regard to an important application of chemistry, an abstract is here given:

"In America the deposits of Bessemer ore are very large, but are greatly exceeded in magnitude by the great phosphoric ore tracts of Pennsylvania, Alabama, Tennessee and Virginia, and it is highly probable that the centre of the steel manufacture of the United States will on this account gradually gravitate southward. The fact that when iron ores are smelted in a blast furnace the whole of the phosphorus they contain will pass into the pig iron produced is too well known to require insisting upon. The only exception is in the case of a few small furnaces which, while producing a particular quantity of iron, will, when working on certain highly phosphoric ores, allow a trifling quantity of phosphoric acid to escape unreduced with the slag, though still producing a highly phosphoric pig iron. Nor does it seem at all probable that in the blast furnace, which is pre-eminently and necessarily a reducing, as opposed to an oxidizing apparatus, there is the slightest chance that the conditions can ever be so altered as to allow of any appreciable removal of phosphorus taking place in the manufacture of pig iron. The attempts that have been made to purify the ore before its introduction into the blast furnace—of which the only partially practicable one is Jacobi's—have also hitherto entirely failed of commercial success. The average proportion of phosphorus in our best known varieties of pig iron may be taken roughly to be as follows: Cleveland, 1.5 per cent.; Scotch, about 1 per cent.; Lincolnshire, 1.25 per cent.; Staffordshire cinder pig, 2.5 per cent.; Staffordshire mine pig, from .5 to 1 per cent.; Northamptonshire, 1.5 per cent. and over. It will thus be seen how far removed all these varieties of pig iron are from the non-dephosphorizing steel-maker's type, which, as we shall see, must not contain appreciably more than one-tenth of 1 per cent., or one part in 1000 of phosphorus.

"The fact that, till the year 1878, in neither of the two great steel-making processes, the Bessemer and Siemens, was phosphorus in the slightest degree removed, is also a matter of universal knowledge. In puddling, on the other hand, it has long been known that from 80 to 90 per cent. of the phosphorus present in the pig iron could be removed without difficulty. Thus, Cleveland pig iron containing 1.5 per cent. of phosphorus will make a puddled bar containing little more than 1-10th of this amount. We should not forget, however, that there is a third great system of steel making—the crucible-steel manufacture, based on the cementation process. As this, however, starts with iron which has already been dephosphorized and decarburized by the puddling or some analogous process, it may be disregarded for the present purpose, with the remark that no better material for the manufacture of cement or crucible steel could be obtained than the highly purified material which it will be shown can be so readily produced by the new Bessemer process. The proportions of the several kinds of steel manufactured in 1880 are estimated by the able Belgian metallurgist and statistician, M. Trasenster, to be as follows: Bessemer, 81 per cent.; Siemens, 16 per cent.; crucible, nearly 4 per cent. It has been said that the presence of more than one part of phosphorus in 1000 of steel is fatal to good quality. This, too, needs some explanation and qualification. Steel may be roughly divided into three classes: hard steels, rail or medium steels, and soft steels. In hard steels containing ½ per cent. of carbon and more, the presence of as much phosphorus as above mentioned is highly prejudicial, rendering the material absolutely unfit for the manufacture of all the better class of tools. In rail steels one part in 1000 is considered in England quite as much as should be tolerated, though when the carbon is as low as ¼ per cent. half as much again may be carried with safety. In fact, in America the average home-made rails do not contain less than 1¼ part of phosphorus per 1000. Many of the Continental rail steels also contain 1¼ per 1000 of phosphorus and more; this being rendered comparatively safe by the fact that foreign engineers prefer rails with a lower content of carbon than is admitted in England.

"The Terrenoire Company and others, taking advantage of the fact that phosphorus is less dangerous in proportion as the amount of carbon in the rails is less, have, indeed, produced rails with 2-1000ths of phosphorus and very low carbon, which in ordinary climates are fairly reliable. For the soft steel and ingot iron containing less than 2-1000ths of carbon, which is now so largely used for manufactures other than rails, such as plates, wire, angles, rivets, sheets, and general purposes, it is also extremely desirable to keep the phosphorus lower than 1 per 1000. For good quality of boiler plates and other special purposes, half this amount should be considered as a maximum. Indeed, it may be taken as a rule that the lower the phosphorus the higher the quality. It is thus seen that in admitting 1-10th of 1 per cent. of phosphorus as the average maximum allowable for good steel, we have, if anything, given a high limit. It is now possible to appreciate more exactly the grounds for the statement that at least 85 to 90 per cent. of the iron ores of Great Britain, and probably nearly the same proportion of the whole known ore deposits of the world, are unavailable for steel-making without a practicable process of dephosphorization. In order to grasp more fully what this means, it may be well to examine into what forms the crude iron which is usually produced is transformed before it passes into consumption. For this purpose, M. Trasenter's figures may be again quoted. Assuming the world's production of pig iron to be 19,700,000 metric tons, approximately 5,250,000 tons are consumed in the manufacture of steel, 9,000,000 tons in the manufacture of iron, and 5,500,000 tons in the production of castings. Again, taking Mr. Jeans' carefully prepared figures for Great Britain, it appears that of the 8,370,000 tons of pig iron made in England, about 2,000,000 tons were employed in the manufacture of steel, and nearly 3,000,000 tons in the manufacture of puddled iron.

Now we have it on the excellent authority of Mr. Edward Williams, the late president of the Iron and Steel Institute, an iron and steel maker of wide and varied experience, that the consumption of coal in manufacturing steel rails from pig iron was, over a series of years, only a trifle over one-third of that employed in the manufacture of iron rails, while the wages cost for manufacturing steel rails is only 28 per cent. of that necessary for the manufacture of iron rails.[1]

"While there is no doubt that the economy of fuel and labor in the manufacture of steel as compared with that of iron is more conspicuous in the case of rail-making than in most other departments of manufacture, the figures above quoted may be taken as closely approximating to the truth in all cases, as, while puddling has, comparatively speaking, stood still for the past ten years, economy in steel-making has made, and is making, rapid progress. How then does it happen that there are 9,000,000 tons of pig iron annually turned into the unquestionably inferior material known as puddled iron, while only 5,500,000 tons are converted into the superior form of steel or ingot iron, particularly when so great an economy of fuel and labor could have been effected by turning the whole into the higher class material? May it not be fairly contended that it is really nothing but the absence of a practical and economical system of dephosphorization that could justify the existence of such an anomaly? It is now proposed to show that there is no reason for its continuance, since the developments and modifications introduced during the last four years enable steel of any desired purity as regards freedom not only from phosphorus, but from silicon and sulphur, to be produced readily and economically from the most highly phosphoric kinds of pig iron.

"The Bessemer process, with concurrent dephosphorization, as now regularly practiced at the Eston Works of Bolckow, Vaughan & Co. (who, under the able guidance of Mr. Windsor Richards, have been the pioneers of the new industry) and 13 other works in France, Belgium, Germany, Austria and Russia, is carried out as follows: The Bessemer vessel is lined with magnesian lime which has been previously subjected to an intense white heat, and so brought to a condition of density, tenacity and hardness as far as possible removed from the condition of the material generally known as well-burnt lime, and more closely resembling granite or flint. This material, which for brevity is known as 'shrunk lime' (as in course of preparation it shrinks to one-half the bulk of ordinary lime) is used either in the form of bricks or in admixture with tar as a rammed or slurry lining, this being substituted for the ordinary silica brick or silicious ganister lining of the hematite process. Before the metal (which may be either employed direct from the blast furnace without intervening remelting, or, if for any reason this is not convenient, may have been remelted in a cupola) is run into the converter, from 15 to 18 per cent. of its weight of common well-burnt lime is thrown into the vessel. The metal is then introduced and the charge is blown in the ordinary way to the point at which the ordinary Bessemer operation is stopped—that is, till the disappearance of the carbon, as indicated by the drop of the flame. The dephosphorizing process requires, however, to be continued for a further 100 to 300 seconds, this period of so-called after-blow, which would be prejudicial both to quality and yield in the ordinary process, being with phosphoric iron, under conditions permitting of the removal of phosphorus, that in which the great bulk of the phosphorus—down, indeed, to its last traces—is removed. The termination of the operation is shown by a peculiar change in the flame, and checked by a sample of the metal being rapidly taken from the turned-down converter, flattened under the hammer, quenched and broken, so as to indicate by its fracture whether the purification is complete. A practiced eye can immediately tell whether or no this is the case. If the metal requires further purification, this is effected by a few seconds' further blowing. The operation is thus, as will be seen, but little different from the ordinary Bessemer process. The differences that have been indicated, viz. the lime lining, the lime addition and the after-blow, are, however, sufficient not only to enable the whole of the phosphorus, which would be otherwise untouched, to be completely removed, but the silicon, of which inconvenient and even dangerous quantities are occasionally left in the regular Bessemer process, is also entirely eliminated, while at least 60 per cent. of any sulphur, also untouched in the ordinary process, which may have been present in the pig, is also expelled. It is found, too, that the once-dreaded phosphorus is of most substantial assistance in securing, by its combustion, the intense heat necessary for obtaining a successful blow and hot metal. If it is desired to produce ingot iron, or a metal differing only from puddled iron by its homogeneity and solidity, the usual recarburizing addition of spiegel is omitted or replaced by ½ per cent. of rich ferromanganese, which represents a considerable economy as compared with the cost of the spiegel necessary for the manufacture of harder steel. The phosphorus is oxidized by the blast, forming phosphoric acid, which, finding itself in presence of two strong bases, oxide of iron and lime, unites with the latter of them to form phosphate of lime, which passes into the slag. Whether or no there is a transitory formation of phosphate of lime, making oxide of iron perform the function of a carrier, is a matter, though interesting theoretically, which it is needless here to discuss.

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[1] Journal of the Iron and Steel Institute, p. 435.

"The order of the removal of the several impurities is well indicated by the diagrams on the wall, for which we are indebted to M. Meier, of Luxembourg, and M. Massenez, of Hoerde. It will here be seen that in the first stage of the operation phosphorus is the substance which is least attacked, while, as the blow advances, and particularly after decarburization, its removal becomes more and more rapid. The contrast between the two operations, it will be observed by reference to diagram 5 (representing an ordinary hematite blow, examined by Mr. Snelus), is most noticeable in the phosphorus curves. In the one, the proportion of this element slightly but distinctly increases from the commencement to the end of the operation. In the other the removal, at first slow, becomes eventually rapid, till ultimately it is entirely at the discretion of the operator whether more than one part in 5000 shall remain. As an instance of the purity of the metal that can be at will produced from pig iron, such as is ordinarily made in Scotland, Staffordshire and Lincolnshire, we may quote analyses made so long ago as the spring of 1880, at Seraing, of steel made at Wittkowitz by the basic process:

	Sil.	Car.	Sul.	Phos.	Man.
Plate No. 1[1]	.000	.04	.01	.008	.29
Plate No. 2	.000	.09	.01	.014	.20
Square bar	.000	.06	.01	.011	.26
Round bar	.000	.07	.01	.000	.26

"It will be seen that these bear comparison with even the phenomenally pure Bessemer steel of Sweden, of which the following is an average anaylsis as given by Akerman:

Sil.	Car.	Sul.	Phos.	Man.
.017[2]	.1	trace	.028	.15
to	to	to	to	to
.029	.3	.01	.031	.36

"The basic Siemens and Siemens-Martin processes are carried out on the same lines as the Bessemer process. The dephosphorization is very complete, but the operation takes about 5 per cent. longer time than when pure material is used; the proportion of lime required is less than in the Bessemer process, and the wear of the basic hearth, with suitable arrangements, is not excessive. The limits of time and your patience render it necessary, for the present, to postpone the detailed consideration of this very interesting and important branch of the subject of dephosphorization, and to confine our attention to the Bessemer process, in which, moreover, most experience has been gained, though many thousand of tons of dephosphorized Siemens steel have been produced, and the process is regularly worked in Continental works.

"It cannot be too clearly understood that among the chief features of the dephosphorizing Bessemer process are, first, its controllability, and secondly, its peculiar suitability for the manufacture of soft steel or ingot iron. Its controllability appears especially to depend upon the fact that while any phosphorus remains it apparently exercises a protective influence on the iron, and so to prevent the tendency to red-shortness, which demands so much skill to avoid in the regular Bessemer process, when soft steel is aimed at. On these points we cannot do better than quote the opinion of Mr. Walrand, who has a long experience of both processes at the great steel works of Creusot. Mr. Walrand expresses himself as follows: 'Those who are occupied in the manufacture of Bessemer steel know how difficult it is to obtain with regularity the extra soft steel employed for boilers in the French navy. Such metal appeared only to be made in the Martin furnace, and even then it was necessary to employ picked material in its manufacture. But by the new Bessemer dephosphorizing process, steels of an extraordinary degree of softness can be obtained with the greatest facility, and at a price less than that of ordinary rail steel. By treating a pig containing from 1.5 to 2 per cent. of manganese, we obtain, after the decarbonization and dephosphorization is finished, a non-oxidized metal which does not contain more than traces of carbon or manganese. If it be desired that the steel should be entirely free from any tendency to red-shortness, we may add from 0.25 to 0.50 per cent. of a rich ferromanganese to remove any traces of oxygenization. The only precaution to be taken to obtain a soft steel is to choose pig (if direct working be employed) which contains sufficient manganese, with 2 per cent. as a maximum, or to make a suitable mixture of pigs, if cupolas be employed. But this will be by no means the only outlet for dephosphorized metal, for up to the present time the high price of soft steel has been the great obstacle which has prevented many people from employing it in construction. But by the new process soft metal can be produced at a less price than ordinary (puddled) iron. There is, therefore, no longer any reason, apart from routine, why steel should not be employed in all cases in place of iron, to which it is so much superior in strength.'

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[1] Journal of the Iron and Steel Institute, 1880, 115. [2] *Ibid.*

"Having endeavored to show that there are strong reasons why the manufacture of puddled iron should be superseded by a process which is not only highly economical, but which produces an ingot or homogeneous product of superior strength, ductility and elasticity, it may be useful to summarize what is being done in the way of manufacturing and preparing for the manufacture of dephosphorized steel. In England, Bolckow, Vaughan & Co. are making weekly about 2300 tons of Cleveland steel, while on the Continent there are 13 works, producing an aggregate of about 7000 tons a week of dephosphorized Bessemer and Siemens steel. The total make is, therefore, at the rate of over 450,000 tons a year. In England there are six converters building for the process, which will probably produce about 3500 tons a week.

"On the Continent there are 25 converters building for the process, with a minimum capacity of 9000 tons a week. Now, as the make of pig iron in England far exceeds that of the whole Continent of Europe, it is clear that we are in this matter allowing our Continental friends to push ahead of us in a way that Englishmen have not hitherto been accustomed to. Whether in this we are wise it is left for others to decide; but one thing is clear, that in all neutral markets our puddled iron will have to contend in future with Continental dephosphorized ingot iron, which can be sold at a lower price and will stand far higher tests. Whether the prediction of Von Tunner (the father of scientific iron manufacture) that the extinction of puddling works is, by the increase of the production of ingot iron by the dephosphorizing method, imminent, is to be proximately realized or not we shall soon have an opportunity of knowing. Lest any apprehension should be felt as to the outlet which is to be found for so much ingot iron, it may be called to mind that we made last year nearly 2,700,000 tons of puddled iron, and imported 90,000 tons in addition. The saving in coal alone, had this been made by an ingot process, would have amounted to nearly 2,000,000 tons, while the smaller worth in converting ingot iron to finished iron would have saved nearly £700,000 worth of material."

NOTES.

Transmission of Gases through Fluids of different Densities. A Lecture Experiment.

If in a given acidified and nearly saturated solution of a salt (I have generally used ferrous sulphate and added a small quantity of sulphuric acid) a piece of zinc is placed, and this solution carefully overlaid with common water, the bubbles of hydrogen appear to meet with considerable resistance at the zone of contact between the two liquids, and from one-third to one-half are reflected downward and to one side. Finally, however, they are again induced by their relative levity to rise; and now scattered, and at a part of the vessel remote from their first ascent, pass through the upper zone and escape into the air.

This phenomenon is again exhibited if upon the second or upper stratum a third liquid is superimposed having a density less than that of water. The appearances at this second zone are however not quite as marked as at the first.

What is the cause of this apparent reflection of the hydrogen bubbles in passing from a denser into a rarer medium? I confess that at present a wholly satisfactory explanation does not occur to me.

Certainly it does not appear reasonable that the circumstance of their meeting with less resistance on entering the rarer medium should occasion a reflection, though by virtue of the reduced difference between the densities of the aeriform body in this second stratum and its enveloping fluid it is conceivable why, perhaps, a less rapid upward movement should result. Is not, however, this influence in favor of a less rapid movement more than compensated for by the diminished resistance of this second medium? Be this as it may, it still cannot explain, I think, why there is a positive reflection of a large part of the bubbles. It might explain a mere retarding in their movement.

In explanation of the above phenomenon it may also be assumed that the bubbles of gas as they rise from the saline liquid into the water above carry with them their envelope, *i. e.* the thin film of solution encircling them. When, therefore, they enter the upper liquid they are too much weighted down to pass at once through the latter, and are therefore detained for an instant. In the meanwhile they are caught by the descending current of the solution, and are for a time carried sidewards and downwards. This downward current is caused as a result of the upward current formed by the rapid ascent of the hydrogen set free by the zinc. I am devising experiments to settle this, if possible, and hope soon to report.

C. GILBERT WHEELER.

Separation of Gallium.

M. LECOQ DE BOISBAUDRAN gives some processes for the quantitative analysis of salts of gallium and the separation of gallium from other metals.

1. *Separation from the alkalies* (*Cs*, *Rb*, *K*, *Na*, *Li*, *and* NH_4). When the proportion of gallium is not very small, the simplest method consists in adding an excess of ammonia to the hydrochloric acid solution and boiling the mixture, adding water from time to time to supply the loss by evaporation, until a piece of litmus paper, previously placed in the liquid, becomes distinctly red. The precipitated oxide of gallium is then filtered off, washed, dried and ignited.

In case there be but a small trace of gallium in the mixture, the boiling solution is treated with cupric hydroxide. The mixture of Ga_2O_3 and copper oxide is then dissolved in excess of hydrochloric acid, the copper removed by sulphuretted hydrogen, and the gallium then precipitated by ammonia as above.

Separation from the alkaline earths (*Ba*, *Sr*, *and Ca*).—If the gallium is in considerable quantity, it can be precipitated directly by the addition of excess of ammonia, followed by long-continued boiling, the oxides of the alkaline earths remaining in solution.

Traces of gallium are separated from large amounts of Ba, Sr, or Ca by means of copper hydroxide, or the greater part of the Sr and Ca and all the Ba may be first removed from the solution by the addition of sulphuric acid and alcohol; if this be done the gallium oxide must be strongly ignited, in order to drive off all the sulphuric acid.

Separation from magnesium.—Prolonged boiling with excess of ammonia answers well. The process with copper hydroxide may be employed in the case of small quantities of gallium mixed with large amounts of magnesium.

Separation from alumina and chromic oxide.—The most convenient process consists in precipitating the gallium by means of potassium ferrocyanide, from a hydrochloric acid solution containing at least a quarter or a third of its volume of concentrated HCl.

When the gallium is present only in very small quantity (less than $\frac{1}{100000}$), one or two days are necessary for its complete precipitation. The precipitate is then filtered off, dried by a gentle heat and ignited; there results a mixture of the oxides of gallium and iron, which can be separated by a method which M. Lecoq de Boisbaudran promises to give shortly. The almost inevitable formation of a little Prussian blue in the strongly acid solution is of no importance, as it only has the effect of slightly increasing the proportion of ferric oxide to be afterwards separated from the oxide of gallium.—(*Comptes Rendus*, 94, 1227.)

R. D. C.

On the Use of Liquefied Gas, and in particular of Ethylene, for the Production of Low Temperatures.

L. Cailletet gives an account of some of his experiments on the use of liquefied gas, particularly ethylene, for the production of low temperatures.

Ethylene is liquefied at +1° by a pressure of 45 atmospheres; its critical point is in the neighborhood of +13°, while that of carbon dioxide corresponds to +31°. These properties led Cailletet to determine whether a more intense cold could not be produced by liquefied ethylene than by liquefied nitrous oxide. In order to compare these temperatures, he made use of a thermometer with an arbitrary scale, filled with carbon bisulphide. When plunged in liquefied ethylene this thermometer indicated a temperature corresponding closely to —105°, far below that caused by liquid nitrous oxide, which is —88°.

The ethylene used in the experiments was prepared in the usual way by heating a mixture of alcohol and concentrated sulphuric acid, and after being purified by passing through cold sulphuric acid and caustic potash solution, to remove the ether and sulphur dioxide, was compressed by means of a powerful pump, designed by M. Cailletet, in bottles previously tested by a pressure of several hundred atmospheres. By this apparatus, ethylene was readily liquefied, but its employment in the liquid state presented serious difficulties, for when the attempt was made to draw off the liquid ethylene from the bottle in the ordinary way, as with nitrous oxide, no trace of liquid was obtained, and it was therefore necessary to devise a special apparatus in order to make use of it as a source of cold.

When liquid ethylene is allowed to escape from the receiver in such a manner that the liquid drops strike directly against the apparatus to be cooled, there is no great loss of the liquid, and the temperature is further lowered by the expansion of the gas not liquefied. These conditions are best realized by fixing the receiver containing the cooled liquid ethylene in an iron support, and attaching to the orifice of the receiver, directed downwards, a tube of glass of 5 or 6 mm. diameter, bent at a right angle. When the stop-cock is opened the compressed gas and the liquid are projected with moderate velocity against the apparatus to be cooled. Liquefied ethylene, by evaporation at the atmospheric pressure, can then produce a cold more intense than has hitherto been realized by any other means; it possesses the advantage, moreover, of remaining liquid and transparent at temperatures at which nitrous oxide and carbon dioxide become solid and opaque.

In experimenting upon the liquefaction of oxygen with the aid of liquid ethylene, M. Cailletet has obtained interesting results differing entirely from those previously observed by him when nitrous oxide was made use of as a source of cold. In the latter case, when the tension of the compressed oxygen, cooled to —88° by means of liquid nitrous oxide, was suddenly diminished by allowing a portion of it to escape, there was produced a light cloud which disappeared immediately on stopping the escape of the gas; when, however, the oxygen was cooled to at least —105° by means of liquid ethylene, there was noticed an appearance of tumultuous ebullition which lasted for quite an appreciable time, and which resembled the sudden projection of a liquid into the tube.

M. Cailletet hopes to produce still lower temperatures by condensing, by means of the apparatus now at his disposal, gases more difficultly liquefiable than ethelyne.—(*Comptes Rendus*, 94, 1224).

R. D. C.

On the Liquefaction of Ozone.

MM. P. Hautefeuille and J. Chappuis have experimented upon the liquefaction of ozone, using for the purpose the apparatus of M. Cailletet mentioned in the preceding note.

A study of the conditions under which a sudden diminution of the tension of a compressed mixture of oxygen determined the formation of a cloud, led them to the conclusion that pure ozone would be little more difficultly liquefiable than carbon dioxide, and they found that the addition of carbon dioxide to the mixture of the gases yielded by compression a liquid colored pale blue, which coloration they attributed to ozone liquefied at the same time with the carbon dioxide. From these facts they concluded that it was possible to obtain ozone in the liquid form, and that the liquid would be strongly colored. Their conclusions have been fully confirmed by experiment, and they have obtained ozone in liquid drops of a deep indigo blue color; this liquid, they state, was preserved for more than 30 minutes under a pressure of 75 atmospheres, its evaporation not being very rapid even under the atmospheric pressure.

The liquefaction was accomplished by compressing to about 125 atmospheres a mixture of ozone and oxygen in the receiver of the apparatus of M. Cailletet. To this receiver was attached an upright capillary tube, the upper part of which was curved back upon itself so that the descending branch could be exposed to a jet of liquid ethylene, by which means it was cooled to a temperature probably below —100°.

On experimenting with a gas containing not more than 10 per cent. by weight of ozone, the gas compressed to 125 atmospheres was not appreciably colored in the ascending branch of the tube, while in the cooled portion the blue coloration was very decided. Upon allowing a portion of the gas to escape suddenly the tube instantly became colorless, and in the drawn-out portion at the end there was formed a drop of deep indigo blue colored liquid; the ozone in the tube being almost totally condensed there, as a further compression to 150 atmospheres did not give an appreciable color to the cooled tube. Once liquefied, ozone will preserve this state for a considerable time in a capillary tube, even at the atmospheric pressure, and can be examined either in the jet of liquid ethylene or by withdrawing the tube from it for a short time. The deep blue liquid diminishes little by little in volume, its vaporization being so slow and its diffusion so rapid that the gas appears colorless above an almost black liquid, and it is only at the moment that the last traces of the liquid disappear that it can be seen that an azure blue gas is produced. The vaporization of the liquid ozone brings the whole apparatus back to its initial state provided the ozone has not been slowly decomposed by the mercury used in compressing the gas.—(*Comptes Rendus*, 94, 1249.)

R. D. C.

On Anhydrous Crystallized Grape-Sugar from Solutions in Water.

Crystallized anhydrous glucose has hitherto been obtained only from alcoholic solutions. ARNO BEHR has recently found that glucose can, under certain conditions, be obtained as the anhydride in crystallized form from solutions in water. This result may be accomplished by putting some crystallized anhydrous glucose in a concentrated aqueous solution of glucose. A good concentration for the purpose is a solution containing 12 to 15 per cent. of water. A temperature of from 30 to 35° C. is apparently the best. The author found, further, that the addition of crystals of anhydrous glucose is not necessary. In fairly pure concentrated solutions of glucose at somewhat elevated temperatures, the crystallization of the anhydride is the normal result. In order, however, to effect a crystallization as uniform as possible, it is advisable to add a little of the dry crystalline powder, though only a very little is necessary. The crystallization of anhydrous glucose is similar to that of cane sugar. The syrup leaves the crystals easily under the influence of centrifugal force. The sweetness of glucose is to that of cane sugar about as 1 to $1\frac{2}{3}$.—(*Berichte der deutsch. chem. Gesell.* **15**, 1104.)

The Atomic Weight of Uranium.

Clemens Zimmerman[1] has prepared metallic uranium by Peligot's method, and determined some of its properties. Its sp. gr. is 18.685, and its sp. heat between 99° and 0° is .02765. The latter number multiplied by 240 gives a product of 6.64, which agrees with the mean atomic heat indicated by Dulong and Petit's law. The controversy between the values 120, 180 and 240 for the atomic weight of uranium is thus settled in favor of the highest, and in accordance with Mendelejeff's classification.

F. W. C.

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[1] Ber. d. deutsch. chem. Gesell. **15**, 847.

Vol. IV [October, 1882.] No. 4.

LIBR UNIVER

AMERICAN CHEMICAL JOURNAL.

DETERMINATION OF ORGANIC MATTER IN POTABLE WATER.[1]

By Prof. J. W. Mallet, F. R. S.

This research was undertaken in compliance with the instructions of a letter from the President of the National Board of Health, written on behalf of the Executive Committee of the Board, and dated Washington, December 29, 1880.

A full report on the objects, in detail, of the investigation, on the methods employed, and the results obtained, has been prepared and placed in the hands of the Board. Pending its publication *in extenso*, the Executive Committee has thought proper to direct that an abstract, covering the principal conclusions reached, shall be published. The following pages present such an abstract.

It was intended to examine carefully the chief processes in use for chemically determining the organic matter, or its constituents, in drinking water, to test the absolute and relative accuracy of the results these processes are capable of yielding, and as far as possible to ascertain the nature and scope of the practical conclusions available for sanitary purposes which may thence be secured.

Three chemists took charge severally of the so-called "combustion process" of Frankland and Armstrong, the "albuminoid-ammonia process" of Wanklyn, Chapman, and Smith, and the "permanganate process," originally suggested by Forchhammer, in the form advocated and minutely described by Tidy. These gentlemen, Mr. W. A. Noyes, Dr. Charles Smart, U. S. A., and Dr. J. A. Tanner, U. S. N., worked independently, the first in the laboratory of the Johns Hopkins University, at Baltimore, by permission of its authorities, the second at the office of the National Board of Health, in Washington, and the third in the laboratory of the University of Virginia. Arrangements were made to have the samples of water for examination collected, and distributed to these three points by myself, so that there should be identity of material submitted to each analyst, and all three analysts should examine their several samples on the same day. Prof. H. Newell Martin, of the Johns Hopkins University, kindly undertook a simultaneous microscropic examination of the waters placed in the hands of the chemists, as also a series of pathological observations on the effect of injecting the waters, concentrated by evaporation at very low temperature, beneath the skin of rabbits, whose temperature and general condition were compared with those of like animals not so treated.

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[1] Preliminary report on the results of an investigation, made by direction of the National Board of Health, as to the chemical methods in use for the determination of organic matter in potable waters.

A large amount of preliminary and special work was done in the early part of 1881, the former chiefly with a view to making the analysts thoroughly familiar with the processes to be tested before coming to the actual tests themselves, the latter on various modifications of the processes in detail, and incidental points in connection with them of sanitary interest. From this work a number of results of considerable interest have been obtained, but their publication will have to be made in their place in the general report.

For the main series of test analyses, the following classes of waters were obtained or prepared:

Class I.—Natural waters, believed from actual use to be of good, wholesome character, including the regular water supply of some of the principal cities of the United States.

Class II.—Natural waters which there seems to be fair ground for believing have actually caused disease on the part of those drinking them. A request for information as to such waters, and for samples of them, was published for several months in the *National Board of Health Bulletin*, and was extensively copied into newspapers and professional journals, and a copious correspondence with physicians and others in various parts of the country was employed to secure such samples, and to sift the evidence as to the supposed connection of the use of each water with the production of disease.

Class III.—Natural waters, of doubtful, but more or less suspected, character. In reference to these the medical evidence was insufficient to justify placing them in Class II.

Class IV.—Artificially prepared waters, made by adding to good, wholesome water, determinate amounts of various infusions of *vegetable* organic matter, of natural origin, and of such kinds chiefly as water for human consumption is liable to be brought in contact with.

Class V.—Artificially prepared waters, made as above, with various forms of *vegetable* refuse from manufacturing or industrial operations.

Class VI.—Artificially prepared waters, as above, made with *animal* (or partly animal) organic matter of natural origin, especially such as are likely to occur in connection with the contamination of drinking water.

Class VII.—Artificially prepared waters, as above, made with *animal* refuse from manufacturing or industrial operations.

Class VIII.—Artificially prepared waters, as above, to which had been added morbid products from certain diseases in the human subject.

Class IX.—Solutions in distilled water, of carefully determined amounts of pure substances of definite chemical composition.

The results obtained from the examination of a large number of samples, representing the above classes of waters, are given in detail in a table in the general report. At present the conclusions reached in the discussion of these results can alone be given.

GENERAL DISCUSSION OF RESULTS.

Degree of accuracy of the three principal processes examined.—This may be looked at in two ways: first, as to the concordance of the results obtained by each process in duplicate or triplicate experiments on the same water; and, secondly, as to the agreement of the results obtained with the actual contents of a particular water when these are quantitatively known.

In the former of these aspects we have to do with such errors as are, practically speaking, fortuitous; in the latter we notice especially the indications of constant errors inherent in the methods used.

Extent of concordance of the results obtained by each process in multiplied experiments on the same water.—This has been tested by taking the mean of duplicate or triplicate determinations, noting the difference between this mean and each of the individual determinations on which it was based, and calculating this difference as percentage on the mean itself. The data for such calculation have been most numerous in the case of the combustion process, since it was considered necessary to make duplicate analyses all through the research, with a number of triplicates. It is the more important that this process should be thus examined, in view of the objection which has been often made to it, that it demands an unusual degree of skill and training on the part of the experimenters. In connection with the extensive work of the English Commission on the Pollution of Rivers, it is to be supposed that many duplicate analyses must have been made by this method, but there has appeared but little in print to show how far these were concordant. The results obtained in the course of the present research are summarized in tables XI, XII, and XIII.

TABLE XI.—*Extent of disagreement of results of multiplied analyses of same water by combustion process.*

	Divergence of individual results from mean, *as percentage on mean.*		
	Greatest.	Least.	Average.
For all waters in classes I to VIII, inclusive, save the few for which there was but one analysis, and those for which there was a known source of error vitiating one of the analyses :[1]			
Organic carbon	24.46[2]	0	4.24
Ditto, rejecting twelve cases in which the divergence was over 10 per cent. (ten of these cases involved very minute absolute quantities of carbon)	9.96	0	2.89
Organic nitrogen	40.00[3]	0	9.48
Ditto, rejecting thirteen cases in which the divergence was over 20 per cent. (ten of these cases involved very minute absolute quantities of nitrogen)	19.82	0	7.09

[1] Representing in all two hundred and sixty-two separate analyses for carbon and two hundred and forty-six for nitrogen. (Some analyses for the latter element were vitiated by uncertainty in the determination of free ammonia, and hence in the amount to be subtracted for this latter.)

[2] Actual difference was less than .3 milligram.

[3] Actual difference was only .04 milligram.

TABLE XI.—*Continued.*

	Divergence of individual results from mean, *as percentage on mean.*		
	Greatest.	Least.	Average.
For the waters in Class IX (solutions of definite chemical substances in known amount)[1]:			
Organic carbon	50.00[2]	.15	9.54
Ditto, rejecting six cases in which the divergence was over 10 per cent. (four of these cases involved very minute absolute quantities of carbon)	7.76	.15	2.81
Organic nitrogen	14.52[3]	0	5.05
Ditto, rejecting five cases in which the divergence was over 10 per cent. (but one of these cases involved a very minute quantity of nitrogen)	9.75	0	2.71
Average of both the above sets of experiments, giving them equal weight:			
Organic carbon (including all cases)	37.23	.07	6.89
Ditto (rejecting in all thirty-six extreme cases, as above)	8.86	.07	2.85
Organic nitrogen (including all cases)	27.26	0	7.26
Ditto (rejecting in all thirty-six extreme cases, as above)	14.78	0	4.90

[1] Representing in all forty-one separate analyses each for carbon and nitrogen. (One determination for each was without a duplicate, and hence had to be rejected from the data for this table.) [2] Actual difference was .035 milligram. [3] Actual difference was .47 milligram.

TABLE XII.—*Extent of disagreement of results of multiplied experiments on same water by albuminoid-ammonia process.*

	Divergence of individual results from mean, *as percentage on mean.*		
	Greatest.	Least.	Average.
For thirteen waters in Classes I to VIII, examined in triplicate :[1]			
Free ammonia	36.05	0	5.91
Ditto, rejecting two cases, involving very minute quantities of free NH_3	19.05	0	2.79
Albuminoid ammonia	8.51	0	2.69
For waters of Class IX (twenty-one in all—all examined in duplicate):[2]			
Free ammonia	5.53	0	1.67
Abuminoid ammonia	14.28	0	6.19
Ditto, rejecting four cases involving very minute quantities of alb. NH	12.79	0	4.56
Average of both the above sets of experiments, giving them equal weight:			
Free ammonia (including all cases)	20.79	0	3.79
Ditto (rejecting two extreme cases, as above)	12.29	0	2.23
Albuminoid ammonia (including all cases)	11.39	0	4.44
Ditto (rejecting four extreme cases, as above)	10.65	0	3.62

[1] Representing thirty-nine separate determinations.

[2] Representing forty-two separate determinations; of course purely negative results are not included in the data for this table.

TABLE XIII.—*Extent of disagreement of results of multiplied experiments on same water by permanganate process.*

	Divergence of individual results from mean, *as percentage on mean.*		
	Greatest.	Least.	Average.
For twelve waters in Classes I to VIII, examined in duplicate:[1]			
Oxygen consumed in one hour[2]	4.70	0	1.09
Oxygen consumed in three hours[3]	4.35	0	.56
For waters of Class IX (twenty-one in all—all examined in duplicate):[4]			
Oxygen consumed in one hour[5]	8.33	0	.62
Oxygen consumed in three hours[6]	6.66	0	1.10
Average of both the above sets of experiments, giving them equal weight:			
Oxygen consumed in one hour	6.51	0	.85
Oxygen consumed in three hours	5.50	0	.83

[1] Representing twenty-four separate determinations.

[2] Including five cases in which divergence was over 1 per cent. (in all these but very little oxygen was consumed).

[3] Including two cases in which divergence was over 1 per cent. (in these very little oxygen was consumed).

[4] Representing forty-two separate determinations. Of course those are not included in the data for this table which showed no oxygen, or but a mere trace, consumed.

[5] Including one case in which divergence was over 1 per cent. (very little oxygen consumed).

[6] Including three cases in which divergence was over 1 per cent. (very little oxygen consumed).

Of the figures given in the last column of Table XI, those which probably represent with most fairness the average departure from the mean of an individual determination by the combustion process[1] are:

For organic carbon . .	2.89 per cent.
For organic nitrogen . .	7.09 "

This goes in part to support the opinion of Tidy[2] that the results of the combustion process are less to be relied on for nitrogen than for carbon.

The results shown for the waters of Class IX are less deserving of attention in this particular respect, since there were but seven different organic substances included, and these specially selected. The reversal of position of the carbon and nitrogen results in this class as compared with the preceding, is partly due to great and variable loss by evaporation of the volatile organic acids, and by dissociation of the salts of amines, &c.

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[1] See Mills' conclusions from a much more limited basis of induction furnished by a few of Frankland's analyses—Jour. Chem. Soc. (Lond.), February, 1878, 58 *et seq.*

[2] Jour. Chem. Soc. (Lond.), January, 1879, 56.

From the last column of Table XII, the figures which probably may most fairly be taken to represent the average divergence from the mean of a single determination by the albuminoid-ammonia process are:

For free ammonia . .	2.23 per cent.
For albuminoid ammonia .	3.62 "

We should naturally expect to find greater irregularity in the evolution of the so-called albuminoid-ammonia, though the conditions of chemical action be made as nearly as possible the same.

As regards the averages in the last column of Table XIII, the consumption of oxygen by the waters in Class IX having been for the most part very small, it seems probable that, for practical purposes, the first figures may best be taken, viz:

For oxygen consumed in one hour .	1.09 per cent.
For oxygen consumed in three hours .	.56 "

showing somewhat greater irregularity in the early stage of the action than later.

It will be seen that on the whole the most closely concordant results were furnished by the permanganate process, and the least so by the combustion process, the albuminoid-ammonia process holding the intermediate position.

Extent of agreement of the results obtained by the different processes with the quantities of organic constituents known to be actually present.—The detailed evidence under this head is given in columns 19 to 25, inclusive, of the last sheet of Table X, in which the results actually obtained on examination of the waters in Class IX (solutions of known amounts of certain organic substances of definite chemical composition) are compared with the amounts of the organic elements really present and the calculated amounts of oxygen required for their complete oxidation.[1] The following summary (in Table XIV) presents the conclusions reached within the limits of these experiments.

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[1] In this calculation hydrogen has been taken as converted into water, carbon into carbon dioxide, and nitrogen as evolved in uncombined form; of course no one would expect any such ultimate results of oxidation from the action of the permanganate as practically applied. Frankland, in a similar calculation (Jour. Chem. Soc. (Lond.), March, 1868, 83), seems to have taken the nitrogen as oxidized to nitric acid.

Table XIV.—*Extent of agreement of results obtained by the different processes with the known chemical character of the waters in Class* IX.

				Amounts obtained, as percentage upon amounts calculated.		
				Greatest.	Least.	Average.
Combustion process:						
Organic carbon				85.	1.	53.
Organic nitrogen (including that of ammonia)				180.	47.	118.
Albuminoid-ammonia process:	Greatest.	Least.	Average.			
Nitrogen of free NH_3[1]	94.	0.	(28.)[2]			
Nitrogen of alb. NH_3[1]	84.	0.	(24.)[2]	95.	0	53.
Permanganate process:						
Oxygen consumed in one hour				13.	0	3.
Oxygen consumed in three hours				16.	0	4.

(In this table, as in the last sheet of Table X, a considerable fraction of 1 per cent. is represented by 1—; an insignificant fraction is considered = 0.)

The figures of this table strikingly indicate certain important defects of the several processes, although they must be looked at in a broad, general way, remembering the small number of organic substances treated, and their special characters.

As regards the combustion process, we find loss of carbon, in all cases considerable, and in some cases very great; with a strong tendency on the whole to excess of nitrogen, which in some cases is very great. It is of course easy to see how, in large measure at least, these errors were caused for some of the samples. Thus, doubtless, free butyric and valerianic acids were formed from their salts, and volatilized with the water during its evaporation; the salts of the amines probably suffered partial dissociation, with volatilization of the bases; and urea was lost after conversion into ammonium carbonate. It may be objected that such substances as these ought not to have been selected. But it is to be remembered that every one of them occurs among the products of putrefactive decay of albuminoid or other organic matter, and hence may fairly be looked for among the constituents of organically polluted water.[3]

[1] Both calculated as percentage on *total* nitrogen present.

[2] These two averages have no real significance.

[3] Fresenius and Scherer have found butyric and propionic acids in the mineral water of Bruckenau and Weilbach. Zeitschrift für anal. Chem. **20**, 3, 325.

The occurrence of loss of organic constituents during the evaporation of water for the combustion process has often been suspected by the critics of that process,[1] and often, though sometimes cautiously, denied by its advocates. Thus Mills has said:[2] "Substantially satisfactory evidence has been adduced that there is no material loss during the evaporation." The experiments now reported prove exactly the reverse of this, and furnish for the first time, as far as I know, direct evidence of the fact that, for some organic substances at least, and those of a kind liable to occur among the products of putrefaction, there *is* material, nay, very great loss.

As regards the frequently presented excess of nitrogen, I am strongly inclined to believe it in part at least due to absorption, during the evaporation of the acidified water, of ammonia *from the atmosphere surrounding the gas flame* and water-bath. Due care was taken as to the general condition of the atmosphere of the room, and it hardly seems possible to account for the error from this source.[3] But any one who has noticed the considerable deposit of ammonium sulphate formed on platinum vessels over an ordinary laboratory lamp or on bells suspended over household gaslights, will readily admit that here is a manifest source of danger. The extent to which ammonia is removed from coal gas at different works, and in the same works at different times, varies no doubt a good deal, but all American gas which I have examined readily shows its presence. With the gas in use at the University of Virginia and the neighboring town of Charlottesville, I find that when not ignited it will in five seconds produce a distinct yellow stain on a drop of the Nessler reagent upon white filtering paper, and, although no doubt much ammonia undergoes combustion when the coal gas itself is burning, a platinum capsule of three inches in diameter, containing water to keep it cool, will, if held over the flame of a Bunsen burner for half a minute, and the outside surface then washed off into a test-glass, yield a liquid which distinctly gives the Nessler reaction for ammonia. During the many hours of the evaporation of a water sample there must occur in the atmosphere about the water-bath a quantity of nitrogen in the form of ammonia which may well be called very large in comparison with the amounts dealt with by the water analyst, and although contact of the contents of the glass dish with this atmosphere is largely cut off by the glass shade, such contact is not entirely prevented, as there is the notch in the rim of the water-bath for the passage of the feed-flask neck. The avidity with which such ammonia as may reach the acid water will be absorbed by it is obvious enough, even though some be afterwards lost by dissociation. The excess of nitrogen observed in the analyses of Class IX seems to be general; even in those cases in which a loss is recorded it will be noticed that this loss is always less than for the carbon of the same substance, and the result is most probably a mere balance between two errors in opposite directions, actual loss of organic nitrogen volatilized in some form during the evaporation of the water, very possibly to even a greater extent than for carbon, and on the other hand absorption of nitrogen as ammonia from the atmosphere.

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[1] Wanklyn asserts in the most positive way the occurrence of loss, but gives no experimental evidence in support of his assertion. (Water Analysis, London, 1879, 190.)

[2] Jour. Chem. Soc. (Lond.), February, 1878, 58.

[3] The most scrupulous pains, too, were taken to guard against leakage of air into the Sprengel vacuum and nitrogen from the cupric oxide, and errors from these sources could scarcely have failed to be detected. They were examined into over and over again.

In reference to the results obtained by the albuminoid-ammonia process, little more is presented than has already been fully discussed in an earlier part of the general report. The total loss of the amine bases by volatilization during the first distillation (with sodium carbonate) results practically, as these bases do not produce the ammonia color with the Nessler reagent, in their nitrogen escaping recognition under the head of either "free" or "albuminoid" ammonia. Here we have a proof that some, at least, of the nitrogenous products of putrefaction are not detected or determined by this process as usually conducted.[1] There is no discrepancy between the results as to these bases here noticed, and that recorded for a triethylamine salt in Table VII of the general report; in this last mentioned case the salt was in contact with alkaline permanganate from the commencement of the distillation.

The results in this Class IX by the permanganate process have mainly the same sort of interest. It has, of course, long been known that, in the words of Tidy,[2] "there are many substances (most of which are crystalline) that are altogether unacted upon, or very slowly acted upon, by the oxygen of permanganate"; but it has been distinctly claimed for this process[1] by the same chemist that "it undoubtedly furnishes us with exact information as to the relative quantities of putrescent and easily oxidizable matter, and of non-putrescent or less easily oxidizable matters, present in the water. The former (viz. the putrescent organic matters) it indicates quantitatively with great accuracy ; the latter (viz. the non-putrescent matters) are scarcely capable of the same exact estimation as the former, for they are bodies for the most part of difficult oxidation." Now here we have some of the definite substances which are actually known to occur among the constituents of putrescent albuminoid matter, and it needs but a glance at the table to see how limited is their oxidation by the cold acid permanganate, and yet how considerable are the differences in behavior of these few substances selected mainly on the same general principle.

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[1] Wanklyn has excepted nitro-compounds and (erroneously) urea, but clearly implies that these are the only exceptions; that the nitro-compounds are without practical importance, and that urea is specially provided for. Water Analysis, London, 1879, 189.

[2] Jour. Chem. Soc. (Lond.), Jan. 1879, 78.

Of course it is not assumed that the figures in Table XIV really represent either the range of absolute error, or the average amount of absolute error, of the different processes as applied to the doubtless very various forms of organic matter liable to occur in natural waters ; these figures do, however, illustrate the existence of sources of absolute error, and by examples taken from the very class of substances which it has been most commonly believed important to detect and determine in water analysis.

Effect on the results by the different processes of varying the extent of dilution of the same organic substances in water.—The evidence in regard to this point is graphically presented in Tables XV, XVI, and XVII.

(These tables will appear with the general report.)

In studying these tables, indications of definite effects on the results of the various processes arising from the degree of dilution of the liquids examined soon become apparent, but seem to be subject to much irregularity. Such irregularity, however, is much reduced by a careful consideration of all the circumstances affecting individual cases. Thus, some of the numerical results of analysis ought to be omitted from consideration as vitiated by known errors, as in the case of albuminoid ammonia determinations in obtaining which the whole of the alkaline permanganate was reduced, or an obviously considerable part of the ammonia was still coming off when the process had to be stopped. In other cases the value of the results is rendered doubtful by the solution examined having been excessively dilute or excessively strong; the relatively greater analytical errors for the former, and for the latter the errors of measurement of very small quantities of the liquid itself, and greater uncertainty as to its uniformity when turbid, tend to make the figures obtained less trustworthy than when intermediate degrees of concentration were involved; Nos. 110 to 118 inclusive represent the former source of abnormal results, such waters as No. 100 the latter. Again, the three solutions containing each form of polluting material in different degrees of dilution were, as has been explained, necessarily examined on different days, and evidence of changes going on in the meantime are to be found in the relative amounts of free and albuminoid ammonia, the character of the dissolved gases, &c. (see for the latter Nos. 83, 84, 85); hence, the *order* in which the three solutions of each group were examined has to be taken into account. Further, the results of one of these tables have often to be considered in their bearing on those of the others, as, for instance, the free ammonia determinations as affecting the value of the figures for organic nitrogen. And, lastly, after having observed the general drift of the errors indicated, we can see in the varying balance of errors of opposite effect an explanation of many apparently exceptional figures.

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[1] *Loc. cit.* 80.

The general results of such detailed study of individual cases agree with those obtained by a simple calculation of averages, omitting from the calculation such figures as on sound grounds of general principle are to be regarded as vitiated for the purpose of this discussion. In the following table the solutions of the seven pure chemicals (Nos. 141 to 161) have been left out on account of the abnormal relations of these (which have been separately discussed) to some of the processes. For the combustion process, two other substances, represented by the dilutions Nos. 101 to 103, and 122 to 124, are omitted, because in the former of these the figures for organic carbon are known to be of very little value, and those for organic nitrogen are entirely valueless in consequence of the uncertain determinations of free ammonia present in large qnantity (which had to be subtracted from the gross results of analysis), while in the latter the very large amount of the free ammonia correction makes the results doubtful. For the albuminoid ammonia process, those determinations of free ammonia originally marked by Dr. Smart as uncertain (by a ?), have been omitted, and those determinations of albuminoid ammonia in making which the regular charge of alkaline permanganate was entirely reduced, requiring an additional charge to be afterwards added, or dilution to be resorted to. For the Kubel form of the permanganate process one or two cases have been omitted, in which the permanganate was entirely reduced, making the result valueless save as an approximation. Rejecting these obviously worthless data, the averages from all others are given in Table XVIII.

TABLE XVIII.

Average results obtained for different dilutions of same solution of organic matter.

	One-fifth per cent. strength.		One per cent. strength.	Five per cent. strength.	
	Calculated.	Obtained.	Assumed.	Calculated.	Obtained.
Combustion process:					
Organic carbon	20.	17.5	100.	500.	549.8
Organic nitrogen	20.	25.2	100.	500.	372.2
Albuminoid-ammonia process:					
Free ammonia	20.	39.9	100.	500.	445.3
Albuminoid ammonia	20.	27.2	100.	500.	257.9
Permanganate process:					
Tidy method—					
Oxygen consumed in one hour	20.	19.7	100.	500.	475.0
Oxygen consumed in three hours	20.	20.0	100.	500.	468.9
Kubel method—					
Oxygen consumed	20.	19.9	100.	500.	475.9

As regards the combustion process, we find distinct confirmation of the existence of the two forms of constant error which have been pointed out as affecting the evaporation.[1] The weaker the solution, or in other words, the larger the quantity of water to be evaporated for a given amount of organic matter, the less is the amount of organic carbon obtained, indicating relatively greater loss of this element. On the contrary, the weaker the solution or the greater the quantity of water to be evaporated, the larger is the figure for organic nitrogen, indicating relatively greater gain of this element from the atmosphere, and probably in some cases less dissociation of ammoniacal salts, when the amount of free ammonia found is considerable. If the usual interpretation of Frankland's C : N ratio be applied, the curious and important result of these sources of error, affecting the two elements in opposite directions, follows, that the more dilute an organically polluted water is, the more animal-like in origin will its polluting material seem to be, while the stronger it is the greater will be the tendency to refer the contamination to a vegetable source; this distortion of the conclusions to be drawn from an examination by the combustion process is manifestly in the opposite direction to that commonly assumed to be safe.

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[1] Compare the results observed by Mills (Jour. Chem. Soc. (Lond.), Feb. 1878, 60) in using evaporating dishes of different diameters. The larger dish gave a rather lower result for carbon, and higher for nitrogen.

In reference to the albuminoid ammonia process, the weaker the solutions are, the higher are the results obtained, both for free and albuminoid ammonia,[1] the influence common to both being probably that of imperfect condensation in the distillation, having a less effect as the quantity of ammonia is smaller. As for the albuminoid ammonia, the lower results obtained from the stronger solutions may be partly due to the smaller proportion borne by the fixed charge of alkaline permanganate to the quantity of organic matter to be acted on. The great irregularity in individual analyses is strongly indicative of a varying balance of errors from different sources. It will be observed that the discrepancy between the calculated figures and those of experiment is greatest for free ammonia in the case of the weakest dilution, while the reverse is true for albuminoid ammonia.

The results of the permanganate process are shown to be much less influenced by varying dilution within the limits involved in these experiments than those of the other processes. In the case of the solutions of greatest strength somewhat smaller figures are obtained for the oxygen consumed than calculation calls for.[2] This is probably due to the fact that for the weaker waters the ordinary fixed charge of permanganate added at the first leaves at the close of the process a relatively larger excess than is present when successive additions of the reagent have been made to a water strong enough to reduce the first charge completely.

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[1] This agrees with Dr. Smart's single experiment on Washington sewage in its original form and diluted. See "remarks" on No. 116 in Table X of general report.

[2] Some indications of a like result may be noticed in a few experiments of Tidy (Jour. Chem. Soc. (Lond.), January, 1879, 80, 81), though the variation in strength of his solutions was not so great, and he himself draws the conclusion that the consumption of oxygen was proportional to the strength.

We must not confound the effect of varying the amount of organic matter in relation to the permanganate by which it is to be oxidized with that of varying greatly, but to the same extent, the degree of dilution of both organic matter and permanganate at the same time. Dr. Tanner's experiments showed that under the latter head a solution of even potassium nitrite might be made so dilute that its action on a correspondingly small quantity of permanganate was rendered very slow.

It may, perhaps, be said in reference to all these experiments on varied dilutions of the same materials, that the several processes under examination are intended for use on water of approximately suitable character for drinking, not on comparatively strong solutions of organic matter, such as many of those I have employed, but the answer to this objection is, that these liquids were taken in order to *exaggerate*, and hence bring to light any defects inherent in the several processes, so far as such depend upon the simple condition of the amount of polluting material in proportion to that of pure water.

SPECIAL CONCLUSIONS AS TO THE COMBUSTION PROCESS.

These may be briefly stated as follows:

1. The combustion itself, carried out according to the directions of Frankland, is a process of great delicacy, and quite satisfactory in its details with proper precautions and in trained hands. There seems to be no advantage in employing any of the various modified ways of determining the gaseous products of combustion which have been proposed instead of gaseous volumetric analysis with the aid of the Sprengel vacuum.

2. The Frankland process is quite within the reach of the manipulative skill of any fairly-trained chemist, but it requires practice, and probably pretty constant practice. It cannot be taken up offhand and even tolerable results obtained at once. From the hands of a person without proper laboratory training, its results are utterly valueless. It is hence better adapted to regular use in the examination of many samples of water in a large public laboratory than to occasional use by a private individual in now and then examining a single water.

3. The defective point in the process is the failure of the evaporation to leave a residue representing the original organic matter of the water. This, which has been hitherto more or less suspected, has been established as a fact by the investigation now reported on. The process being conducted according to the directions of its authors, there are two constantly present errors, varying, but usually important in amount, namely, loss of carbon,[1] and gain of nitrogen from the atmosphere, the latter probably partly balanced by loss of that originally present in the water. These errors are relatively greatest when the quantity of organic matter in the water is small.

4. These errors, affecting unequally the carbon and nitrogen, are liable to alter the statement of C : N. ratio,[2] and hence to distort the sanitary conclusions usually drawn therefrom.

5. The result for organic nitrogen, as obtained by the combustion process, is also affected indirectly by the errors connected with the determination of the ammonia ("free ammonia"), as the nitrogen belonging to this has to be subtracted from the gross result. The existence of such errors, as from imperfect condensation of the ammonia, progressive decomposition of urea and other amides, &c., has been pointed out in previous pages of this report, and will be referred to in the conclusions as to the albuminoid-ammonia process.

6. There is a further indirectly operative cause of error as to the nitrogen, arising from the varying loss of ammonia by dissociation of its salts during the evaporation of the water. Frankland recognizes the necessity of a correction for this, which correction he makes depend upon the amount of ammoniacal salts present, but it is almost certain that the time occupied in the evaporation will also influence the extent of loss by dissociation. Error from this source will in most cases be very small, but may affect to a not unimportant extent the result for *organic* nitrogen.[3]

7. The combustion process involves special difficulties in the presence of nitrates, for which difficulties no completely satisfactory

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[1] In connection with this a number of Dr. Smart's experiments are noteworthy, in which the distillate for free ammonia furnished evidence, by its haziness and greenish color, distinct from that which the Nessler reagent should have yielded, that volatile organic matter was present.

[2] In Prof. W. R. Nichols' Report on the Boston Water Supply (Fourth Annual Report of Boston Water Board, 1880), variations of the C : N ratio, extending from a given value to one three or three and a half times as great are observable for the Cochituate water within a few weeks, and still greater variations for the Mystic water.

[3] Examples are furnished by Frankland of analyses in which the ammonia correction is very large in comparison with the organic nitrogen.

remedy is as yet proved to have been found. M. W. Williams' mode of applying the copper-zinc couple for this purpose is deserving of more precise quantitative examination than it has yet received. The simultaneous presence in a polluted water of urea with nitrites and nitrates presents a case of peculiar difficulty involving several sources of error.

8. The formation of sulphuric acid during the evaporation of the water with sulphurous acid seems to be of more frequent occurrence than has hitherto been recognized. Mr. Noyes seems to think that to this source—small amounts of cupric sulphate being formed on mixture of the residue with cupric oxide—may perhaps be attributed the occasional presence, as noticed by Frankland, of traces of free oxygen among the gaseous products of combustion. This occurrence of sulphuric acid in the water residue, even in minute amount, is undoubtedly much to be deprecated, though its effect, at any rate on the carbon determinations, has not seemed to be as great as might have been expected.

9. The combustion process in its present form cannot be considdered as "determining" the carbon and nitrogen of the organic matter in water in a sense to justify the claim of "absolute" value for its results which has been denied to those of all other methods. It is but a method of approximation, involving sundry errors, and in part a balance of errors.

10. There is, however, good ground for believing that in many, perhaps most, cases its results for organic carbon may, with proper precautions, be made more valuable than the indications of the permanganate process, and its results for organic nitrogen in like manner more valuable than the indications of the albuminoid-ammonia process.

SPECIAL CONCLUSIONS AS TO THE ALBUMINOID-AMMONIA PROCESS.

These may be briefly summed up as follows:

1. In the determination of both "free" and "albuminoid" ammonia there is a loss, which may be quite considerable, resulting from imperfect condensation of the ammonia during distillation. This loss varies in amount with the precise conditions under which the distillation is conducted, especially with the efficiency of the cooling apparatus and the time occupied in the process.

2. In the case of waters containing urea, and also other amidated bodies, such as the leucine and tyrosine occurring among the pro-

ducts of putrefactive decay, some ammonia is so easily formed from these substances by boiling with sodium carbonate, or even without this addition, that it is impossible to distinguish sharply between pre-existing "free" ammonia (of ammoniacal salts), and that formed by the action of alkaline permanganate, the so-called "albuminoid" ammonia. This source of error as to the free ammonia reacts, as has been noticed above, upon the result for organic nitrogen by the combustion process.

3. There is no satisfactory evidence in favor of Wanklyn's view that in distilling with alkaline permanganate, definite and simple fractions of the nitrogen of organic matter are given off as "albuminoid" ammonia. Such results may be varied at pleasure, for most, if not for all substances, by slight modification of the conditions under which the distillation is conducted.

4. If the distillation with alkaline permanganate be carried out as usual, in accordance with Wanklyn's instructions, it frequently happens that the nitrogenous organic matter is so gradually acted upon as to make the ending of the process indefinite; ammonia is still coming off when the distillation has to be stopped in consequence of the contents of the retort being nearly reduced to dryness. In such cases an unknown fraction of the possible amount of albuminoid ammonia fails to be collected, and is but vaguely indicated by the sign + after the figures recorded.

5. There is evidence that in some cases nitrogenous organic matter is volatilized during the distillation for free ammonia, which, if it had been retained, would have yielded up its nitrogen as albuminoid ammonia; not affecting the Nessler reagent, such nitrogenous matter escapes detection under either head.

6. The albuminoid-ammonia process proper, *i. e.* the distillation with alkaline permanganate and determination of the ammonia evolved, is admittedly simple and easily carried out with very little preparatory training.

7. The value of the results by this process depends more upon watching the *progress* and *rate* of evolution of the ammonia than upon determining its total amount.

8. Taking the results by this process as recorded, we find a good deal of general similarity between the figures for albuminoid ammonia and those for organic nitrogen (by the combustion process), but with frequent discrepancies of varying extent, such as prevent the one being taken as the accurate measure of the other. See Tables XIX and XX, further on.

SPECIAL CONCLUSIONS AS TO THE PERMANGANATE PROCESS.

The chief points worthy of attention are the following:

1. The results obtained by the Tidy method (using the acidified permanganate at common temperature) and by that of Kubel (operating at the boiling point) differ irregularly from each other, the latter usually giving much higher figures, as was to be expected, but the ratio between the results by the two methods varies much in different cases.

2. On the whole, there seems usually to be a nearer approach to proportionality with the quantities of organic carbon[1] found by the combustion process on the part of the results afforded by the Kubel process than on that of the Tidy results, but to this there are some very notable exceptions. See, on this point, Tables XIX and XX, further on.

3. In a good many instances the results obtained by the Kubel method are, contrary to the general rule, lower than those afforded by the Tidy method. This seems to be due, in all probability, to loss of organic matter by volatilization with the escaping steam from the boiling liquid before time has been afforded for action on the permanganate.[2] An examination of all the results obtained for Nos. 131, 132 and 133, and several other cases, gives good ground for believing this to be the case. Of course, a similar loss may have occurred in other instances, but not to the extent of reversing the general rule as to the results by the Kubel process being larger than those by the method of Tidy; and this may in part explain the absence of any uniform ratio between the figures yielded by those two modifications of the permanganate process.

4. The results obtainable by the Tidy process are liable to variation with the atmospheric temperature prevailing at the time the process is applied.

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[1] This appears to be the proper way of comparing the results of the permanganate with those of the combustion process. The former process is clearly concerned much more with carbon than nitrogen, if oxygen be usually at all consumed by nitrogen. It is not easy to admit the soundness of the logic with which Tidy (Jour. Chem. Soc. (Lond.), Jan. 1879, 94-97) points to the concordance of results, by the permanganate and combustion processes, and the disagreement with both these of the results by the albuminoid-ammonia process, and hence apparently infers that the two former are trustworthy, and the last not so. He uses the *sum of organic carbon and nitrogen* to represent the results by the combustion process, and as the carbon forms generally much the larger part of this, he naturally arrives at an agreement with the results of the process mainly depending on the oxidation of carbon, and disagreement with those of the process evolving nitrogen as ammonia.

[2] It is worthy of remark that the largest number of cases among natural waters of the Kubel process giving a lower result than that by the Tidy process occur among the waters believed to be *dangerous, i. e.* Class II.

5. The amount of oxygen consumed by a specimen of water is probably in all ordinary cases much below that required for complete oxidation of the organic matter present, and does not stand in any fixed ratio thereto; it cannot be taken as a measure either of the organic carbon or of the total organic matter. Nevertheless, a distinct general resemblance may be traced between strongly marked results, high or low, as the case may be, for the consumption of oxygen on the one hand, and organic carbon (by the combustion process) on the other; and closer agreement is observable in regard to waters of generally similar character.[1]

6. The permanganate process is capable of giving more valuable information in regard to a water by watching the *progress* and *rate* of the oxidation of organic matter present than by any single determination of the absolute amount of oxygen consumed in a given time.

7. For such observation of the progress of oxidation the two determinations prescribed by Tidy, viz. of oxygen consumed in one hour and in three hours, respectively, are not sufficient, nor is the latter period of three hours long enough to indicate the general behavior of the water with acid permanganate.

GENERAL REMARKS ON OTHER CHEMICAL DETERMINATIONS.

1. The determinations of total solids left on evaporation, of the loss on ignition of this solid residue, and even of chlorine, in the series of varied dilutions of identical or nearly identical liquids, show discrepancies which illustrate the comparative roughness of the methods by which these results were obtained when very small quantities have to be dealt with.[2] The evaporation of 100 cc. of water usually left a residue, the absolute weight of which was but a few milligrams, and a very little difference in the dryness attained, or in the atmospheric deposition on the surface of the platinum capsule, involved relatively large errors in the result. Even the volumetric processes for chlorine are far inferior in delicacy to those employed for the organic constituents.

2. As regards the results for nitrites and nitrates, the coincidence seems to be worth noting, which is often presented between alkaline

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[1] In accordance with the remarks of Frankland: "Water Analysis," p. 55.

[2] It is true that Dr. Smart took no very special pains with these determinations, which were looked upon merely as incidental to the main object, checking to some extent the information as to the general character of each water. Still, this part of the work was done with fully average ordinary care.

reaction of a water and the occurrence of these salts in considerable or large quantity, suggesting as this does a recollection of the conditions under which nitrates are produced on the large scale in the decay of nitrogenous organic matter. The coincidence, however, is not always observable, nitrites and nitrates occurring pretty largely in some cases without alkaline reaction, while in other instances (as Nos. 89, 90 and 91, containing the washings from starch manufacture) there was alkaline reaction, and also much nitrogenous matter, but no nitrites or nitrates. Mr. Noyes has drawn my attention to the fact that in the waters containing large amounts of nitrates, ammonia appears in but small proportion; hence ammonium nitrate seems to be rare, the basic constituent being rather for the most part non-volatile—no doubt calcium, magnesium, or one of the alkaline metals; this is worth notice in relation to possible reduction to nitrite and consequent loss of nitrogen in the combustion process. The view of Frankland that nitrites are producible in water by the reducing action of organic matter upon nitrates[1] is clearly sustained by the results for Nos. 64 and 65, these representing a water originally containing nitrates to which different amounts of an infusion of hay had been added; it seems by no means established that nitrites are *always* developed by reduction, some of Dr. Tanner's experiments which have been reported indicating that on the contrary these salts may be produced by oxidation, which, if it go on, leads to the formation of nitrates. Frankland's view, also, that nitrates are not found in waters deficient in dissolved oxygen, is in general accordance with the results obtained in this investigation, though there are a few instances—Nos. 20, 27, 43, and notably 33—in which nitrates are present to a considerable extent in waters with less than a full proportion of free oxygen in solution.

3. The experiments with tannin simply serve to show how utterly worthless is this "group-reagent" of Kämmerer for the purpose for which he has advocated its use.

4. The general series of analyses of the dissolved gases confirms what has been said on previous pages of the general report as to the number of varying conditions which influence the results in this direction—oxidizability of organic matter present, temperature, extent of exposure to the atmosphere, and interchange with it in both directions of gaseous constituents. In a number of cases the

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[1] "Water Analysis," pp. 28 and 42.

consumption of dissolved oxygen, and production in its place of carbon dioxide from the carbon of organic matter is very obvious, but the extent to which this is found going on varies greatly, and is masked by the escape to a greater or less extent of the latter gas and reabsorption from the air of the former. The conclusion of Weyl and Zeitler,[1] from a few experiments, that the quantity of free oxygen in solution does not bear any fixed ratio to the quantity of acidified permanganate decolorized by a water, is sustained by many of the specimens in the main series, as for instance, Nos. 60 to 80, inclusive. Nevertheless, it may be well to include an examination of the dissolved gases in the study of any water in regard to which the fullest chemical information is desired. In such a case the examination ought to be made with the least possible interval of time after collection of the sample, and preferably on the spot where the sample is taken, with observation of the temperature of water and air.

MICROSCOPICAL AND PATHOLOGICAL RESULTS.

Feeling my own incompetence properly to discuss these, I prefer to leave them to speak for themselves, except so far as Professor Martin has, as quoted in a previous part of the general report, given his views as to the methods employed and the general significance of the facts recorded—these views having been formed, however, while he still was ignorant of the history of the individual waters.

It may be said, I think, that the microscopic and culture observations indicate at the same time the real importance of connecting with a chemical examination of water a study in competent hands of its microscopic organisms both as to number and kind, and also the difficulty often presented, either by the sparseness or more frequently the abundance of these organisms, in fairly estimating their average relation to the mass of the water. This difficulty is superadded, of course, to the imperfection of our knowledge as to the effects upon human health of some closely allied—even hardly distinguishable—organisms, of dangerous and harmless associations, and of perhaps the same organism in different stages of its life history. The probable general significance of certain large classes of organized forms seems, however, well established, and well worthy of attention.

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[1] Zeitschr. f. phys. Chem. **5**, 10 (1880).

It may also be said of the pathological experiments with rabbits, that, opening up as they do a new and almost untried field of research, they show the great complexity of conditions to be encountered, the necessity of careful attention to details, and of multiplying and varying such experiments as far as possible, and the caution which must be exercised in drawing generalized conclusions from them; but on the other hand the results so far obtained, many of which individually are exceedingly suggestive, seem to indicate that real value attaches to this method of investigation, not in the direction proposed by Emmerich (as a part of the ordinary examination of a drinking-water, in order to determine directly its wholesomeness or the reverse), but as the means in part of arriving at trustworthy grounds for the interpretation of chemical and microscopical results.

(*To be continued.*)

Contributions from the Chemical Laboratory of Harvard College.

XXIV.—ON CERTAIN TETRASUBSTITUTED PROPIONIC ACIDS.

By Henry B. Hill and Charles F. Mabery.

In a previous communication[1] one of us has already mentioned the fact that the dibromacrylic from mucobromic acid, unlike the dichloracrylic acid of Wallach, takes up a molecule of bromine with readiness and forms a tetrabrompropionic acid. We were led to undertake a more complete study of the tetrasubstituted propionic acids, especially with the hope that the study of those containing two different halogens might throw some light upon the position of the halogen atoms in the disubstituted acrylic acids formed from mucobromic and mucochloric acids. After our investigations were concluded, Mauthner and Suida[2] published in the Proceedings of the Vienna Academy a paper entitled "Ueber gebromte Propionsäuren und Acrylsäuren," in which they anticipate us in the publication of a portion of our work. Since they were perfectly well aware that, in studying derivatives of a substituted acrylic acid which they asserted, although without adequate proof, was identical with that obtained from mucobromic acid, they were trespassing upon ground which one of us had already fully reserved, we think it advisable, although it involves a certain amount of repetition, to give our results in full, more especially since we are able to correct their work in several important particulars.

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[1] This Journal **3**, 116; and Proceedings American Academy, **16** (N. S. viii), 197.

[2] Sitzungsberichte der kk. Akademie Wien, **83**, 273.

Tetrabrompropionic Acid.

Tetrabrompropionic acid can readily be made by the addition of bromine to dibromacrylic acid at ordinary temperatures.[1] We have prepared it by adding to a solution in chloroform the calculated amount of bromine. On standing, the addition product gradually separates, often in large, well-formed prisms. The amount of the product thus obtained was about 90 per cent. of the theoretical yield. After recrystallization from chloroform the substance was dried over sulphuric acid.

I. 0.5480 gram substance gave 0.1837 gram CO_2 and 0.0286 gram H_2O.

II. 0.1775 gram substance gave 0.3432 gram AgBr.

	Calculated for $C_3H_2Br_4O_2$.	Found.	
		I.	II.
C	9.23	9.14	...
H	0.51	0.58	...
Br	82.04	...	82.28

Tetrabrompropionic acid crystallizes in prisms of the triclinic system, which melt at 125–126°. It is very soluble in alcohol or ether, readily soluble in hot chloroform, carbonic disulphide or benzol, and separates in crystals as these solutions cool. In ligroin it is sparingly soluble. Under water it melts at a very low temperature to a colorless oil which dissolves freely on heating.

For a crystallographic study of the substance we are indebted to Dr. W. H. Melville.

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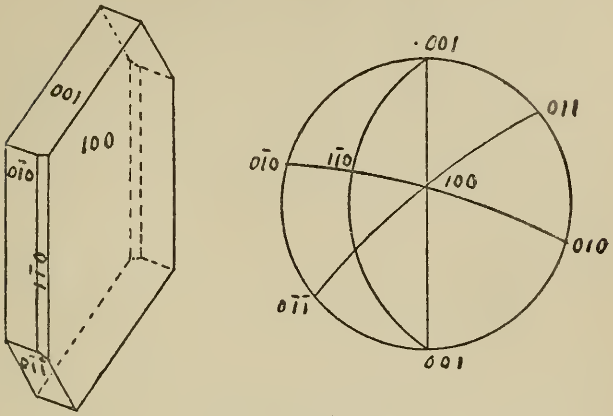
[1] Mauthner and Suida assert that the dibromacrylic acid will take up no bromine in the cold. They prepared tetrabompropionic acid by heating to 100° with undiluted bromine. That the bromine is very readily taken up one of us first mentioned several years ago (Berichte der deutsch. chem. Gesellsch. 12, 657).

CRYSTALLINE FORM OF TETRABROMPROPIONIC ACID.



Triclinic System.

Forms, [100] [010] [001] [011] [110].

Elements: Macrodiagonal $a = 1.507$
Brachydiagonal $b = 1$
Vertical axis $c = 0.934$
Angles of axes $XY = 94°59'$
$XZ = 104°28'$
$YZ = 74°20'$

Angles between Normals.

	Observed.	Calculated.
100 and 010	$= 88° 48'$	Fundamental angles.
010 " 011	$= 56° 3'$	
011 " 001	$= 48° 51\frac{1}{2}'$	
100 " 011	$= 77° 21\frac{1}{2}'$	
100 " 110	$= 57° 25'$	
100 " 001	$= 77° 1'$	76° 21′

Argentic Tetrabrompropionate, $AgC_3HBr_4O_2$. Argentic nitrate added to a solution of the acid in dilute alcohol precipitates the silver salt in clustered needles, which may further be increased in quantity by the cautious addition of ammonic hydrate. The salt is extremely unstable, forms argentic bromide on warming, and blackens rapidly in diffused light.

1.2182 gram of the salt dried over H_2SO_4 gave 0.4744 gram AgBr.

	Calculated for $AgC_3HBr_4O_2$.	Found.
Ag	21.78	22.38

Baric Tetrabrompropionate, $Ba(C_3HBr_4O_2)_2 . 2H_2O$. An aqueous solution of the acid dissolved baric carbonate rapidly in the cold, and if the solution was not warmed there was no noticeable decomposition. On spontaneous evaporation at ordinary temperatures the barium salt was left in clusters of flattened needles. When dried by exposure to the air they contained two molecules of water, which they lost over sulphuric acid.

I. 0.7239 gram of the air-dried salt lost over H_2SO_4 0.0272 gram H_2O.

II. 0.7087 gram of the air-dried salt lost over H_2SO_4 0.0259 gram H_2O.

	Calculated for $Ba(C_3HBr_4O_2)_2 . 2H_2O$.	Found. I.	Found. II.
H_2O	3.79	3.76	3.66

0.6756 gram of the salt dried over H_2SO_4 gave on ignition with H_2SO_4 0.1742 gram $BaSO_4$.

	Calculated for $Ba(C_3HBr_4O_2)_2$.	Found.
Ba	14.97	15.16

Calcic Tetrabrompropionate, $Ca(C_3HBr_4O_2)_2$. The calcium salt, made by neutralizing an aqueous solution of the acid with calcic carbonate and allowing the solution to evaporate spontaneously, crystallized in needles which proved to be anhydrous. The salt freed from moisture by pressure did not materially lose in weight when exposed to the air, and when air-dried lost nothing over sulphuric acid.

I. 0.5065 gram of the salt dried over H_2SO_4 gave on ignition with H_2SO_4 0.0888 gram $CaSO_4$.

II. 1.0886 gram of the salt dried over H_2SO_4 gave 0.1850 gram $CaSO_4$.

	Calculated for $Ca(C_3H_2Br_4O_2)_2$.	Found. I.	Found. II.
Ca	4.89	5.16	5.00

When a solution of baric tetrabrompropionate was heated baric bromide was formed, carbonate dioxide escaped, and at the same time the liquid became turbid through the separation of a colorless oil.[1] On distilling the liquid the oil passed readily over with steam, and since from the method of its formation there could be little doubt that it was tribromethylen, for identification it was immediately converted into its dibromide by the addition of bromine. The crystalline addition product which was thus obtained when purified by recrystallization melted at 53° and gave on analysis a percentage of bromine which showed it to be pentabromethan.

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[1] Mauthner and Suida assert that this decomposition also takes place on long standing at ordinary temperatures. They were therefore able to isolate no salts. We have never observed any decomposition in the cold. *Loc. cit.* p. 284.

0.1696 gram substance gave 0.3766 gram AgBr.

Calculated for C_2HBr_5.	Found.
94.12	94.48

This decomposition may therefore be expressed by the equation:

$$Ba(C_3HBr_4O_2)_2 = BaBr_2 + 2CO_2 + 2\,C_2HBr_3.$$

By the action of an alcoholic solution of potassic hydrate upon tetrabrompropionic acid a molecule of hydrobromic acid is removed, and there results the tribromacrylic acid melting at 118° which we have already described.[1] Dr. W. H. Melville kindly made a crystallographic study of the crystals which we obtained, and established their identity with those he had previously examined, which were prepared by the addition of bromine to brompropiolic acid. A description of the crystalline form of tribromacrylic acid Dr. Melville presents in a separate communication.

α Dichlorbrompropionic Acid.

In studying the dichloracrylic acid made from mucochloric acid W. Z. Bennett and one of us found that even at 100° it would not take up bromine when dissolved in chloroform.[2] Subsequently it appeared from the experiments of C. W. Andrews that the substituted propionic acid could readily be made by the action of undiluted bromine, although circumstances at the time prevented a detailed study on his part. As a precise characterization of this addition product seemed of interest we undertook its preparation and investigation.

Pure dichloracrylic acid melting at 85-86° was heated with a molecule of bromine for several hours at 100°. The almost colorless product of the reaction was pressed thoroughly with paper and purified by crystallization, at first from carbonic disulphide, and finally from chloroform. When dried over sulphuric acid this substance gave on analysis percentages agreeing closely with those required by the formula $CH_2Cl_2Br_2O_2$. In the indirect determination of the halogens we used the extremely convenient and accurate method recently described by Mr. L. P. Kinnicutt.[1]

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[1] This Journal **3**, 178; and Proceedings American Academy **16** (N. S. viii), 216. Mauthner and Suida assign to the barium and calcium salts of this acid, prepared by them from tetrabrompropionic acid, formulae differing greatly from those which we formerly established by our analyses. Since their determinations were made with small quantities of material, we have not thought it necessary to make further analyses in support of our formulae.

[2] This Journal **3**, 172; and Proceedings American Academy, **16** (N. S. viii), 211.

I.[2] 0.8124 gram substance gave 0.3550 gram CO_2 and 0.0665 gram H_2O.

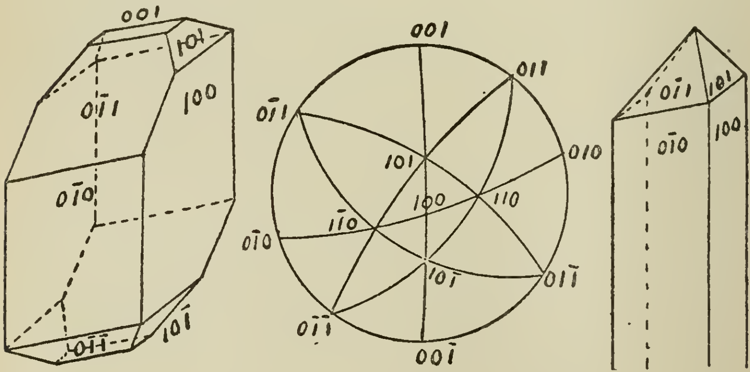
II. 0.1715 gram substance gave 0.3775 gram AgCl+AgBr.

III. 0.4790 gram substance gave 1.0559 gram AgCl+AgBr. From this by reduction was obtained 0.6887 gram Ag.

	Calculated for $C_3H_2Cl_2Br_2O_2$.		Found.		
			I.	II.	III.
C	11.96		11.91	...	...
H	0.67		0.90	...	...
Cl	23.59	76.74	...	76.93	23.77
Br	53.15				52.90

This *a* dichlordibrompropionic acid crystallizes in well-formed triclinic prisms, which melt at 94–95°. It is readily soluble in water, alcohol, or ether; in carbonic disulphide, chloroform, or benzol it dissolves less freely. From a solution in carbonic disulphide it could be obtained by slow evaporation in well-formed crystals, whose study was kindly undertaken by Dr. W. H. Melville.

Crystalline Form of *a* Dichlordibrompropionic Acid.



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[1] This Journal 4, 22; and Proceedings American Academy, 17 (N. S. ix), 91.

[2] These analyses were made by Mr. Andrews.

Triclinic System.

Forms, [100] [010] [001] [101] [011] $[10\bar{1}]$ $[01\bar{1}]$; [110] and $[1\bar{1}0]$ often present.

[1] Elements: Macrodiagonal a = 1.023
Brachydiagonal b = 1
Vertical axis c = 1.052
Angles of axes XY = 91°
XZ = 76° 31½′
YZ = 108° 52′

Angles between Normals.

	Observed.	Calculated.
100 and 010 =	93° 37′	Fundamental angles.
100 " 101 =	52° 58′	
010 " 011 =	34° 57′	
010 " 101 =	77° 19′	
101 " 011 =	58° 46′	
100 " $10\bar{1}$ =	38° 32′	38° 41′
011 " 001 =	35° 21′	35° 52′
001 " $0\bar{1}1$ =	55° 45′	55° 30′
100 " 011 =	101° 3′	100° 39′
100 " $0\bar{1}1$ =	98° 49′	98° 38′
101 " 101 =	87° 34′	88° 20′
$10\bar{1}$ " $01\bar{1}$ =	50° 32′	50° 30′

Argentic α Dichlordibrompropionate, $AgC_3HCl_2Br_2O_2$. The silver salt falls, on the addition of argentic nitrate to an aqueous solution of the acid, in flattened jagged needles which are readily decomposed by heat. They could, however, be dried over sulphuric acid without any essential decomposition, as is shown by the following analysis:

0.4885 gram of substance gave by precipitation with HBr 0.2231 gram AgBr.

	Calculated for $AgC_3HCl_2Br_2O_2$.	Found.
Ag	26.46	26.23

Baric α Dichlordibrompropionate, $Ba(C_3HCl_2Br_2O_2)_2$. The barium salt we made by neutralizing a cold aqueous solution of the acid with baric carbonate. On evaporation at ordinary temperatures it crystallized in long branching needles, which when dried by exposure to the air did not lose materially in weight over sulphuric acid, and contained a percentage of barium corresponding to the anhydrous salt.

---

[1] Through an error the ratios of the fundamental parameters were originally given in the Berichte der deutsch. chem. Gesellsch. **14**, 1680: a : b : c = 1.034 : 1 : 1.062.

I. 0.5069 gram of the air-dried salt gave 0.1606 gram $BaSO_4$.
II. 0.5239 gram of the air-dried salt gave 0.1676 gram $BaSO_4$.

	Calculated for $Ba(C_3HCl_2Br_2O_2)_2$.	Found. I.	II.
Ba	18.59	18.58	18.81

The barium salt is decomposed by warming, its solution giving products similar to those obtained in the same way from tetrabrompropionic acid. This decomposition, however, we have not as yet studied further.

β *Dichlordibrompropionic Acid.*

Although dibromacrylic acid assumes a molecule of bromine so readily, we found at first great difficulty in preparing the corresponding addition-product with chlorine. If chlorine gas is passed into melted dibromacrylic acid it is gradually taken up and the melting-point of the acid is slowly changed. After long-continued action a considerable quantity of the dichlordibrompropionic acid is formed, but so contaminated with oily by-products that its purification is a matter of some difficulty. This addition of chlorine is, however, rapidly and neatly accomplished if the reaction is allowed to proceed in direct sunlight at 100°. When at this temperature the melted acid becomes nearly solid with separating crystals of the addition-product, the chlorination is interrupted. The product which we obtained in this way from pure dibromacrylic acid melting at 85–86° was purified by crystallization first from carbonic disulphide and finally from chloroform. On analysis it gave the following results:

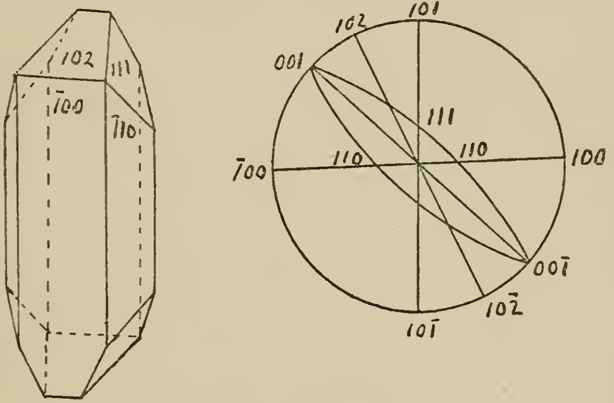
I. 0.5183 gram substance gave 0.2335 gram CO_2 and 0.0431 gram H_2O.

II. 0.1547 gram substance gave 0.3400 gram AgCl+AgBr. From this by reduction was obtained 0.2214 gram Ag.

	Calculated for $(C_3H_2Cl_2Br_2O_2)$.	Found. I.	II.
C	11.96	12.13	...
H	0.66	0.92	...
Cl	23.59	...	23.37
Br	53.15	...	53.21

This β dichlordibrompropionic acid crystallizes in oblique prisms which melt at 118–120°, and in its behavior with solvents closely resembles the α acid. In water, alcohol or ether it dissolves very easily, but with somewhat more difficulty in carbonic disulphide, chloroform, or benzol. The solution in carbonic disulphide gave by slow evaporation well-developed crystals whose elements Dr. W. H. Melville kindly determined.

CRYSTALLINE FORM OF β DICHLORDIBROMPROPIONIC ACID.



Monoclinic System.

Forms, [100] [110] [111] [102].

Elements: Clinodiagonal a = 2.393
Orthodiagonal b = 1
Vertical axis c = 1.731
Angle of axes XZ = 46° 9′

Angles between Normals.

			Observed.	Calculated.
110	and	$\bar{1}10$ =	60° 11′	Fundamental angles.
111	"	$\bar{1}10$ =	42° 24½′	
111	"	110 =	40° 33½′	
$\bar{1}00$	"	$\bar{1}10$ =	59° 53′	59° 54½′
111	"	$\bar{1}11$ =	120° ½′	119° 56′
100	"	111 =	88° 57′	88° 47′
102	"	$\bar{1}10$ =	102° 21′	102° 23′
102	"	110 =	78° 5′	77° 37′
102	"	111 =	63° 44′	63° 42½′

The difference between the α and β acids was further confirmed by a study of the silver and barium salts.

Argentic β Dichlordibrompropionate, $AgC_3HCl_2Br_2O_2$. The silver salt is precipitated in the form of short, thick, pointed prisms when argentic nitrate is added to an aqueous solution of the acid. It is readily decomposed by heat, but may be dried for analysis over sulphuric acid.

0.4950 gram of the salt gave on precipitation with HCl 0.1731 gram AgCl.

	Calculated for $AgC_3HCl_2Br_2O_2$.	Found.
Ag	26.46	26.31

Baric β Dichlordibrompropionate, $Ba(C_3HCl_2Br_2O_2)_2 . 2H_2O$. The barium salt which we made by neutralizing an aqueous solution of the acid with baric hydrate, crystallized on spontaneous evaporation of its solution in long radiating needles which were very soluble in cold water. When dried by exposure to the air the salt proved to contain two molecules of water which it lost over sulphuric acid.

I. 1.6201 gram of the air-dried salt lost over H_2SO_4 0.0705 gram H_2O.

II. 1.5443 gram of the air-dried salt lost over H_2SO_4 0.0731 gram H_2O.

	Calculated for $Ba(C_3HCl_2Br_2O_2)_2 . 2H_2O$.	Found.	
		I.	II.
H_2O	4.66	4.35	4.74

0.8236 gram of the salt dried over H_2SO_4 gave 0.2616 gram $BaSO_4$.

	Calculated for $Ba(C_3HCl_2Br_2O_2)_2$.	Found.
Ba	18.59	18.69

These results prove that the α and β dichlordibrompropionic acids described are essentially different.

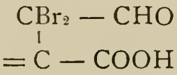
	Dichlordibrompropionic Acid.	
	α	β
System of Crystallization	Triclinic.	Monoclinic.
Melting-point.................	94–95°	118–120°
Barium salt..................	$Ba(C_3HBr_2Cl_2O_2)$	$Ba(C_3HBr_2Cl_2O_2)_2 . 2H_2O$.

The barium salt was readily decomposed by warming its aqueous solution. Baric chloride and carbonic dioxide were formed together with a colorless oil which undoubtedly was a dibromchlorethylen. With bromine this oil gave a solid addition product, which, however, we have not as yet prepared in quantity sufficient for complete purification and identification.

XXV.—ON THE CONSTITUTION OF THE SUBSTITUTED ACRYLIC AND PROPIONIC ACIDS.

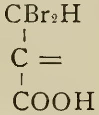
By Henry B. Hill.

Within a few years the number of substituted acrylic and propionic acids known has been largely increased, and yet the constitution of but few of these can be said to be satisfactorily established. In a previous communication I was led to adopt provisionally for mucobromic acid the formula—



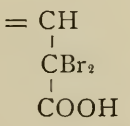
$$\begin{array}{l} CBr_2 - CHO \\ | \\ = C - COOH \end{array}$$

which explained its connection with maleic acid, in whose molecule the researches of Fittig had shown the probable existence of a dyad carbon atom. The structure of the related dibromacrylic acid was then naturally expressed by the formula—



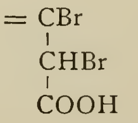
$$\begin{array}{l} CBr_2H \\ | \\ C = \\ | \\ COOH \end{array}$$

against which at the time nothing more convincing than a belief in its improbability could be urged. The relations which Andrews and I have shown to exist between this same acid and two different tribrompropionic acids prove, however, that this formula is incorrect. An acid with this structure could be formed from but a single tribrompropionic acid, and must of necessity give this same tribrompropionic acid by the addition of hydrobromic acid. The same objection also applies with equal force to the other two conceivable formulae for dibromacrylic acid which contain dyad carbon—



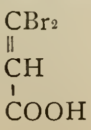
$$\begin{array}{l} = CH \\ | \\ CBr_2 \\ | \\ COOH \end{array}$$

and



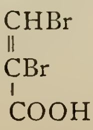
$$\begin{array}{l} = CBr \\ | \\ CHBr \\ | \\ COOH \end{array}$$

and these must consequently be rejected. There remain therefore for the acid in question but two possible formulae—



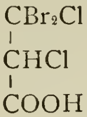
$$\begin{array}{l} CBr_2 \\ \| \\ CH \\ | \\ COOH \end{array}$$

and



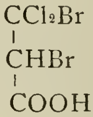
$$\begin{array}{l} CHBr \\ \| \\ CBr \\ | \\ COOH \end{array}$$

The formation of two isomeric dichlordibrompropionic acids by the addition of chlorine to the dibromacrylic acid and of bromine to the analogous dichloracrylic acid, as Mabery and I have shown, would seem again to be decisive in favor of the first of these formulae, since its adoption would give—



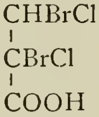
$$\begin{array}{l} \mathrm{CBr_2Cl} \\ | \\ \mathrm{CHCl} \\ | \\ \mathrm{COOH} \end{array}$$

and



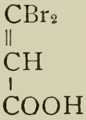
$$\begin{array}{l} \mathrm{CCl_2Br} \\ | \\ \mathrm{CHBr} \\ | \\ \mathrm{COOH} \end{array}$$

as the structure of the two isomeric dichlordibrompropionic acids, while the second formula would give in either case the same compound—



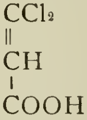
$$\begin{array}{l} \mathrm{CHBrCl} \\ | \\ \mathrm{CBrCl} \\ | \\ \mathrm{COOH} \end{array}$$

Although it was by no means impossible that a molecular rearrangement had taken place in one of these two reactions, still it seemed improbable, since the reactions were apparently neat, and in the treatment with chlorine, where such a change would be more naturally expected, no bromine could be detected in the escaping chlorine. On the other hand the adoption of the formulae—



$$\begin{array}{l} \mathrm{CBr_2} \\ \| \\ \mathrm{CH} \\ | \\ \mathrm{COOH} \end{array}$$

and

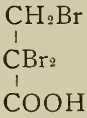


$$\begin{array}{l} \mathrm{CCl_2} \\ \| \\ \mathrm{CH} \\ | \\ \mathrm{COOH} \end{array}$$

for the derivatives of mucobromic and mucochloric acids presented difficulties quite as serious. In the first place the dichloracrylic acid of Wallach had been proved beyond all doubt to be different from that which Bennett and I had described by a comparison of the crystalline form of the two acids, and it would follow then that Wallach's acid could not have the formula he assigned to it. The formation of an acid with different structure from chloralid could, however, be explained upon the assumption that the chlorpropiolic acid was the first product of the reduction, and that this passed, on the one hand by the addition of hydrogen, into the β chloracrylic acid, and on the other hand formed dichloracrylic acid by addition in the subsequent treatment with strong hydrochloric acid which

Wallach prescribes.[1] Although this hypothesis was far from satisfactory, it seemed to me hardly more improbable than that a similar molecular rearrangement had taken place in the reaction which had come under my own observation.

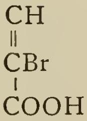
Still another difficulty was to be found in the formation of the dibromacrylic acid in question from the tribrompropionic acid melting at 92°, which, if the ordinarily accepted formula for the latter—



$$\begin{array}{c} CH_2Br \\ | \\ CBr_2 \\ | \\ COOH \end{array}$$

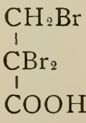
were correct, would prove the incorrectness of the formula assumed. I was at first unable to attach any great importance to this argument, inasmuch as the constitution of the monobromacrylic acids was extremely uncertain. For although the discovery by Wallach of the *β* monobromacrylic acid melting at 115° had rendered the constitution of the *α* and *β* monobromacrylic acids of Tolens extremely doubtful, it by no means proved their identity.

Erlenmeyer has, however, recently shown[2] that the *α* and *β* acids of Tollens, as well as their potassium salts, crystallize in identical forms, and the structure of the tribrompropionic acid melting at 92° is therefore put upon quite another footing. Since the same (*α*) monobromacrylic acids can be made from *α* dibrompropionic and also from its isomer, the *α β* dibrompropionic, it follows that this acid must have the structure—



$$\begin{array}{c} CH \\ \| \\ CBr \\ | \\ COOH \end{array}$$

and the tribrompropionic acid made from it by the addition of bromine must of course have the corresponding form—



$$\begin{array}{c} CH_2Br \\ | \\ CBr_2 \\ | \\ COOH \end{array}$$

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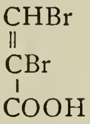
[1] Annalen der Chemie, **193**, 7.

[2] Berichte der deutschen chemischen Gesellschaft, **14**, 1867.

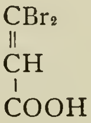
Since the formulae with dyad carbon are in this case excluded, there remains for the dibromacrylic acid in question only the structure—



$$\begin{array}{l}\mathrm{CHBr}\\ \| \\ \mathrm{CBr}\\ | \\ \mathrm{COOH}\end{array}$$

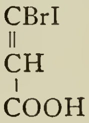
Although this conclusion is directly at variance with the results which Mabery and I obtained in the study of the dichlordibrompropionic acids, it must be confessed, I think, that it is probably correct. Still, since its adoption presents undoubted difficulties, I shall endeavor to bring more direct experimental evidence as to its correctness.

The dibromacrylic acid of Fittig and Petri, which, as Mabery and I have shown, can be made from brompropiolic acid, would naturally have the form—

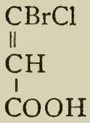


$$\begin{array}{l}\mathrm{CBr_2}\\ \| \\ \mathrm{CH}\\ | \\ \mathrm{COOH}\end{array}$$

and the acids made in the same way containing two halogens the corresponding—

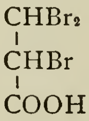


$$\begin{array}{l}\mathrm{CBrI}\\ \| \\ \mathrm{CH}\\ | \\ \mathrm{COOH}\end{array}$$



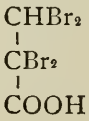
$$\begin{array}{l}\mathrm{CBrCl}\\ \| \\ \mathrm{CH}\\ | \\ \mathrm{COOH}\end{array}$$

The tribrompropionic acid melting at 118° would be written—



$$\begin{array}{l}\mathrm{CHBr_2}\\ | \\ \mathrm{CHBr}\\ | \\ \mathrm{COOH}\end{array}$$

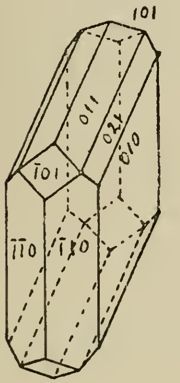
and the tetrabrompropionic acid would have the form—

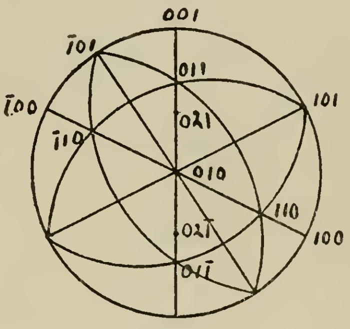


$$\begin{array}{l}\mathrm{CHBr_2}\\ | \\ \mathrm{CBr_2}\\ | \\ \mathrm{COOH}\end{array}$$

XXVI.—CRYSTALLINE FORM OF TRIBROMACRYLIC ACID.

By W. H. Melville.





Monoclinic System.

Forms, [010] [110] [011] [101] [ī01] [021]; the last three forms being rarely observed.

Elements: Clinodiagonal a = 0.502
Orthodiagonal b = 1
Vertical axis c = 0.559
Angle of axes XZ = 64° 29½′

Angles between Normals.

	Observed.	Calculated.
010 and ī10	= 65° 38′	Fundamental angles.
010 " 011	= 63° 14′	
011 " 110	= 57° 35′	
ī10 " īī0	= 48° 42′	48° 44′
010 " 021	= 44° 41′	44° 45′
021 " 011	= 18° 33′	18° 29′
011 " 0ī1	= 53° 33′	53° 32′
011 " ī01	= 42° 25′	42° 23½′

Since[1] Dr. F. Becke's results of the determination of the same crystals do not appear to be reconcilable with the above, a comparison is important. The forms *r* (110) *l* $(1\bar{1}0)$ when referred to the crystals which I have examined, correspond to [021], and *o* $(\bar{1}11)$, *u* $(\bar{1}\bar{1}1)$ would, if present, occur as the prism [120]. Among the many sets of crystals submitted to me I have never observed the prism [120]. The following table shows a few of the angles both actual and hypothetical, assuming that the crystals are monoclinic in form, when compared with Becke's corresponding measurements.

---

[1] Sitzungsberichte der kaiser. Akad. der Wissensch. **83**, 286, 287, Wien, 1881.

Monoclinic.	Becke.
$(010)\wedge(021)=44^\circ\ 41'$	$44^\circ\ 42'=$ *br*
$(021)\wedge(0\bar{2}1)=90^\circ\ 38'$	$91^\circ\ 11'=$ *rl*
$(0\bar{2}1)\wedge(0\bar{1}0)=44^\circ\ 41'$	$44^\circ\ 13'=$ *bl*
$(010)\wedge(\bar{1}20)=47^\circ\ 45\tfrac{2}{3}'$	$47^\circ\ 19'=$ *bu*
$(\bar{1}20)\wedge(\bar{1}\bar{2}0)=84^\circ\ 28\tfrac{2}{3}'$	$84^\circ\ 55'=$ *ou*
$(\bar{1}\bar{2}0)\wedge(0\bar{1}0)=47^\circ\ 45\tfrac{2}{3}'$	$48^\circ\ 10'=$ *bo*
$(010)\wedge(020)=44^\circ\ 41'$	$44^\circ\ 27\tfrac{1}{2}'=$ mean of *br* and *bl*
$(010)\wedge(120)=47^\circ\ 45\tfrac{2}{3}'$	$47^\circ\ 44\tfrac{1}{2}'=$ " " *bu* " *bo*

The following measurements, which were obtained from a single crystal, appear to establish conclusively the system of crystallization as monoclinic.

Zone [010, 110]

$$\begin{array}{l}
(110)\wedge(010)=65^\circ\ 33' \\
(010)\wedge(\bar{1}10)=65^\circ\ 44' \\
(\bar{1}10)\wedge(\bar{1}\bar{1}0)=48^\circ\ 28' \\
(\bar{1}\bar{1}0)\wedge(0\bar{1}0)=65^\circ\ 52\tfrac{1}{2}' \\
(0\bar{1}0)\wedge(1\bar{1}0)=65^\circ\ 35' \\
(1\bar{1}0)\wedge(110)=48^\circ\ 44' \\
\hline
\qquad 359^\circ\ 56\tfrac{1}{2}'
\end{array}$$

Zone [010, 011]

$$\begin{array}{l}
\left.\begin{array}{l}(010)\wedge(021)=44^\circ\ 41' \\ (021)\wedge(011)=18^\circ\ 30'\end{array}\right\}\ 63^\circ\ 11' \\
(011)\wedge(0\bar{1}1)=54^\circ\ \ 5' \\
(0\bar{1}1)\wedge(0\bar{1}0)=62^\circ\ 56' \\
\hline
\qquad 180^\circ\ 12'
\end{array}$$

$$\begin{array}{l}
(1\bar{1}1)\wedge(011)=122^\circ\ 32\tfrac{1}{2}' \\
(011)\wedge(\bar{1}10)=\ 57^\circ\ 18\tfrac{1}{2}' \\
\hline
\qquad 179^\circ\ 51'
\end{array}$$

$$(0\bar{1}1)\wedge(\bar{1}\bar{1}0)=\ 57^\circ\ \ 2\tfrac{1}{2}'$$

The crystal face (011) was somewhat imperfect, so that the reflected image was extended in width. Hence, the angles between (0$\bar{1}$1) and adjacent planes are rendered uncertain, but only by the small value of 7′ or 8′. All the other faces gave exceedingly sharp reflections.

From these considerations upon the system in which tribromacrylic acid crystallizes, it will appear that we have to deal with a question of small differences, and that in consequence of the very prominent monoclinic habit, we are justified in making these crystals monoclinic, and not triclinic, as Becke has determined them.

DETERMINATION OF BORACIC ACID.

By Edgar F. Smith.

When a solution of manganese sulphate is added to one of borax, and to this mixture an equal volume of alcohol, there separates rapidly a white flocculent precipitate of manganese borate, MnB_4O_7, insoluble in the alcoholic liquid. The excess of manganese sulphate remains in solution, and can readily be determined in the filtrate from the borate after the expulsion of the alcohol. To ascertain whether the above might be available quantitatively, the following solutions of definite strength were prepared and the experiments recorded.

1. A solution of manganese sulphate, made by dissolving 3 grams of anhydrous $MnSO_4$ in 250 cc. H_2O. 10 cc. of this solution would then correspond to .0600 gram $MnSO_4$.

2. Potassium permanganate solution of such strength that 18.5 cc. were equivalent to 10 cc. of I or 1 cc. $KMnO_4 = .00324$ gram $MnSO_4$.

3. Borax solution: 10 grams well crystallized borax dissolved in 1 litre of H_2O.

The manner of conducting each experiment was as follows: To 10 cc. of the borax solution were added 10 cc. $MnSO_4$ solution and an equal volume of strong alcohol. The whole was well mixed, allowed to stand, carefully covered, for one half-hour, when the manganese borate was filtered rapidly (best with a suction pump), and washed well with alcohol. The filtrate and washings were placed in a platinum or porcelain dish and evaporated to dryness on a water-bath. The residual manganese was then determined according to Volhard's method[1] by dissolving it in water, adding zinc sulphate, then heating to almost boiling, and carefully running in potassium permanganate until the liquid assumed a pink color. The quantity of manganese sulphate thus found and deducted from the whole amount of the salt added, gave a difference representing the manganese sulphate which had combined with the borax. After calculating the amount of manganous oxide to which the sulphate, found by difference, is equivalent, the following equations were employed:

$MnO : 2B_2O_3 :: \text{am't } MnO : \text{corresponding am't } B_2O_3\ (x)$;

and

Orig. sub. 10 cc. borax solution : $x :: 100 : y$ (per cent. B_2O_3 in 10 cc. of the borax solution).

Experiments.

Number of Anal.	Borax solution used.	$MnSO_4$ solution added.	No. cc. $KMnO_4$ requ'd for excess of $MnSO_4$	$MnSO_4$ in excess.	$MnSO_4$ in combination with B_2O_3.	Per cent. found of B_2O_3.
1	10 cc.	10 cc.	6.4 cc.	.0207 gram	.0393 gram	36.44
2	"	"	6.1	.0198	.0402	37.27
3	"	"	6.3	.0204	.0396	36.71
4	"	"	6.3	.0204	.0396	36.71
5	"	"	6.5	.0210	.0390	36.16
6	"	"	6.4	.0207	.0393	36.44
7	"	"	6.5	.0210	.0390	36.16
8	"	"	6.4	.0207	.0393	36.44
9	"	"	6.2	.0201	.0399	36.99
10	"	"	6.3	.0204	.0396	36.71
11	"	"	6.3	.0204	.0396	36.71
12	"	"	6.4	.0207	.0393	36.44
13	"	"	6.5	.0210	.0390	36.16
14	"	"	6.3	.0204	.0396	36.71
15	"	"	6.4	.0207	.0393	36.44
16	"	"	6.3	.0204	.0396	36.71
17	"	"	6.5	.0210	.0390	36.16
18	"	"	6.4	.0207	.0393	36.44

The calculated percentage of B_2O_3 in borax is 36.60, and from the experimental results it will be observed that the method can be successfully applied in the analysis of soluble borates.

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[1] Annalen der Chemie, **198**, 318.

In estimating the boracic acid in insoluble borates, as tourmaline, the following course was pursued. The finely pulverized substance was fused with a weighed quantity of pure sodium carbonate, the fused mass exhausted with water, and to the filtrate containing all the sodium borate, together with some sodium silicate and aluminate, was added an amount of pure ammonium sulphate molecularly equivalent to the sodium carbonate. The solution was then digested until all the ammonia was expelled and the volume of the liquid largely reduced. Any silicic acid or aluminum hydrate which had separated was now filtered off, and the precipitate thoroughly washed with hot water. The solution, again reduced in volume and containing only the borate and sulphate of sodium and excess of ammonium sulphate, was mixed with a definite amount of a manganese sulphate solution (strength previously determined), alcohol added, and after standing one half-hour the borate was removed by filtration, the filtrate evaporated to dryness and the residue carefully ignited to expel the ammonium salt. The manganese sulphate left was dissolved in water, and the same procedure as indicated in the preceding experiments was carried out.

In a specimen of tourmaline from New York the boracic acid found by this method was 9.70 per cent. Another portion of the same material with Marignac's method[1] yielded 10 per cent. B_2O_3. In another tourmaline (locality unknown) two determinations by this method gave 6.55 per cent. B_2O_3 and 6.32 per cent. B_2O_3, while with Marignac's method the amount obtained was 6.80 per cent. B_2O_3.

In some instances upon evaporating the alcoholic solution preparatory to determining the excess of manganese sulphate, brownish flocks separated. These were always dissolved in a little sulphuric acid and then evaporated to dryness.

The writer is under many obligations to Messrs. N. Wiley Thomas, S. B., and W. H. Jarden, S. B., for their assistance in the execution of the details of the above method.

MUHLENBERG COLLEGE, ALLENTOWN, PA., *June* 26, 1882.

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[1] Zeitschrift für analyt. Chemie, **1**, 405.

Contributions from the Chemical Laboratory of Rutgers College.

VII.—ON THE REDUCTION OF FERRIC SOLUTIONS.

By Peter T. Austen and Geo. B. Hurff.

Although numerous volumetric methods have been proposed and used for determining iron, there seems to be none that possesses the simplicity, accuracy and elegance of the titration with potassium permanganate. In the analysis of iron ores by the use of this method, however, there are a few steps which are still open to improvement.

The remarkable discovery of Zimmermann,[1] that the addition of manganese sulphate to solutions of ferrous chloride entirely prevents the liberation of chlorine on the addition of potassium permanganate, thus making it possible to titer directly in a chlorhydric acid solution, has relieved the analysis of iron ores of one of its most irksome steps, the conversion of the chlorhydric acid solution into the sulphuric acid solution preparatory to reduction and titration with potassium permanganate.

The only remaining objection has been that the reduction of the ferrous solutions is liable to be unsatisfactory, either from incompleteness, danger of loss, or the length of time demanded. The reduction by zinc is objectionable because the zinc is liable to be impure, containing carbon or iron. A control determination of the iron can of course be made, and the amount introduced into the analysis deducted, but this is a method never advisable in analysis if it can be avoided, and in this case also increases the amount of work. If the solution is heated, oxidation easily takes place at the end of the reduction when all the zinc has been dissolved, while if an excess of zinc is used it takes time to dissolve the excess. If the excess is not dissolved, metallic iron may be precipitated.[2] Rose-Finkener[3] suggest having the solution dilute and hanging a little stick of zinc in it by means of platinum wire, but it is doubtful if this method is very practical. The use of zinc dust as recommended by R. Drown[4] appears to us to be open to the objection just stated in regard to ordinary zinc, viz. that it often contains iron, thus rendering control determinations, deductions and extra labor necessary. It is claimed for amalgamated zinc and platinum as an advantage that only pure zinc is dissolved, the impurities not passing into solution. A weighty objection to this method is, however, that so much time is lost by it. The reduction in this way always takes several hours; in fact, one recent text-book[1] directs twenty-four hours. Magnesium reduces well, but has the disagreeable property of floating on the surface. The reduction with hydrogen sulphide[2] requires a tedious evaporation.

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[1] Ber. d. d. chem. Ges. **14**, 779.

[2] Mitscherlich, Zeit. anal. Chem. **2**, 72.

[3] Rose, Quant. Anal. 1871, 100.

[4] Zeit. anal. Chem. **18**, 98.

It was our endeavor, therefore, to find some method by which ferric solutions could be quickly reduced and which would require no corrections. The following procedure was found to answer admirably.

The ferric chloride solution, which should contain about 5–10 cc. of free chlorhydric acid and about 0.1 gram of metallic iron in 100 cc., is placed in a 300 cc. flask with a long neck, diluted to 200 cc. and heated nearly to boiling. The heat is then removed, and a saturated solution of sodium sulphite is added in small amounts (about one cc. at a time) till 15–20 cc. in all have been used. While adding the sulphite, it is well to give the ferric solution a revolving motion by gently twirling the flask. The solution becomes colorless, showing that all the ferric chloride is reduced to ferrous chloride. The sodium sulphite which we use is obtained by recrystallizing the pharmaceutical article, and forms beautiful crystals which are perfectly free from iron. As soon as the solution of the sulphite has all been added, a rubber stopper and tube[3] are inserted, the pinch-cock *b* opened, and the liquid heated to boiling and kept at a brisk boil.

It is of course necessary that the last traces of sulphurous acid should be entirely expelled before titration, since any of it remaining would be oxidized by the permanganate and counted as iron. To ascertain if the steam is entirely free from sulphurous acid it is allowed to pass into a test-tube containing about 50 cc. of water to which a little sulphuric acid and a drop of potassium permanganate solution have been added. If there is the slightest trace of sulphurous acid in the steam the liquid will at once be decolorized. If the steam is allowed to pass for some time through this solution of permanganate, it will decompose it, but this does not interfere in any way with the sharpness of the test. As soon as the test shows that the sulphurous acid has all been driven off, the end of the tube is washed off with a little hot water, the heat removed and the pinch-cock *b* closed. The end of the tube is allowed to dip into a beaker of cold distilled water. As soon as the flask has cooled enough to have a vacuum within it, which generally occurs in a few minutes, the clip is opened and the cold water allowed to run in in portions so as to thoroughly wash out the tube. The flask is allowed to fill till the liquid stands at about the beginning of the neck. The clip is then closed, the right-hand tube removed and the contents of the flask cooled[1] under the tap. The manganese sulphate is next added and the titration proceeded with.

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[1] Cairns' Manual of Quant. Anal., p. 45.

[2] Fresenius, Quant. Anal., last Am. ed., p. 279.

[3] Fresenius, Quant. Anal., last Am. ed., p. 268, Fig. 51. In our apparatus, the right-hand tube is bent at about an inch from its junction with the rubber connection.

The above method of procedure works as well with sulphuric acid solutions as with chlorhydric acid solutions. The reduction and titration together take from fifteen to twenty minutes. A number can of course be run at the same time. The following experiments show the accuracy of the method:

Subs. taken.	Weight. taken.	Per ct. of Fe. found.	Per ct. of Fe. calc.	Difference.
Ammonium-Iron Alum,	1	11.529	11.618	—0.089 per ct.
Do.	1	11.649	"	+0.031 "
Ammonium-Ferrous Sulphate,	1	14.291	14.285	+0.006 "
Do.	1	14.291	"	+0.006 "

In another series of experiments 0.2 gram of pianoforte wire was dissolved in dilute chlorhydric acid, diluted to about 150 cc., oxidized with permanganate, the chlorine boiled off and then reduced in the manner described above. The titrations required the same number of cc. of permanganate as the same amount of the same iron used in setting the standard of the permanganate, viz. 16.5–16.6.

If iron alone is to be determined in an iron ore, it is not necessary to separate the silica when the ore is decomposed by chlorhydric acid. The very finely pulverized ore is simply boiled with concentrated chlorhydric acid till decomposed, the resulting liquid and silica washed into a flask and the solution reduced and titered as described. When it is necessary to use a flux it is advisable to separate the silica.

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[1] To obtain sharp results by Zimmermann's method it is necessary that the solution should not be warm.

VIII.—NOTE ON THE PRECIPITATION OF STANNIC OXIDE FROM SODIUM STANNATE.

By Peter T. Austen.

When a solution of sodium stannate is acidified, stannic hydrate is precipitated according to the formula,

$$SnO\,(ONa)_2 + H_2SO_4 = SnO\,(OH)_2 + Na_2SO_4.$$

The precipitate dissolves on addition of an excess of the precipitant. The precipitated stannic hydrate is voluminous, flocculent and gelatinous, resembling aluminic hydrate. So far as I have been able to ascertain, no other decomposition of the stannate, than in the manner indicated, has been effected.

I was surprised to find that, on passing a stream of carbonic acid through a strong solution of sodium stannate containing an excess of sodium hydroxide, a dense, heavy, and rapidly subsiding precipitate of stannic oxide was formed, the reaction being

$$SnO\,(ONa)_2 + CO_2 = SnO_2 + Na_2CO_3.$$

The same precipitation occurs when, instead of carbonic acid, the solution of sodium stannate is boiled with pulverized sodium hydrogen carbonate. In this case the reaction is

$$SnO\,(ONa)_2 + 2NaHCO_3 = SnO_2 + H_2O + 2Na_2CO_3.$$

When dry, the precipitated SnO_2 forms a heavy white extremely fine powder. The reaction affords an excellent method of producing stannic oxide in quantity.

New Brunswick, N. J.

ON THE DETERMINATION OF THE FLASHING POINT OF PETROLEUM.

By [illegible] T. Stoddard.

If the best method [illegible] determining boiling points gave trustworthy results only w[illegible] size and shape of the retort, quantity of liquid and distance from surface of liquid to the vapor delivery tube conformed to certain rigid specifications—the results varying many degrees with a change in any one of these conditions—we should feel not only that a method demanding such precision in apparatus and manipulation left much to be desired in these particulars, but also that the determinations obtained under such arbitrary conditions could be themselves but arbitrary and undeserving the name of true boiling points.

And yet until quite recently the best apparatus devised for finding the flashing point of petroleum presented similar and even more numerous disadvantages.[1] The flashing point as given by these instruments depends upon the size and shape of the oil holder, the quantity of oil, the means of ignition, and distance of the flame or spark from the surface of the oil, as well as upon a number of minor conditions. Agreement in the determinations of a given oil by means of a given tester demands skillful and painstaking manipulation; and agreement of different testers can apparently be secured only by selecting one as arbitrary standard and adopting conditions in the others which shall give corresponding results.

The attempt has evidently been made to simulate in these testers the conditions presented in the oil reservoir of a quietly burning lamp. But these conditions vary in every lamp, and in the same lamp at different times; moreover, it is not only in lamps as properly used and the cans and storage tanks of kerosene that explosions occur. Safety is insured only when we know that under no *possible* conditions, at the temperature to which it is liable to be exposed, can the oil evolve inflammable vapors. We should be able to determine the *minimum* flashing point, and the method should be as independent of external conditions as that employed for finding the boiling point.

The first suggestion of a principle by which this could be accomplished is due to V. Meyer.[2] It is saturation of air with vapor of the oil. Recognizing the promise of this principle, I have studied the methods proposed for its application, paying particular attention to that recently devised by Liebermann.[3]

In the method proposed by Meyer, as well as in the elaborate and clever apparatus of Haass,[4] the saturation of air with vapor is effected by shaking the oil in a closed vessel. Both are dependent for reliable results upon the interval of time allowed between the shaking and the testing. The shaking repeated from degree to

[1] Cf. Engler and Haass, Z. an. Chem. **20**, 1.

[2] Wagner's Jahresb. 1879, 1175, and Z. an. Chem. **20**, 28.

[3] Z. an. Chem. **21**, 321.

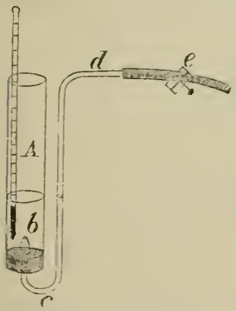
[4] Z. an. Chem. **20**, 29.

degree is an unpleasant feature of these methods. The apparatus of Haass can not be made in the laboratory and is expensive, costing, complete, 60 marks.

Liebermann's apparatus and method present none of these disadvantages. The air is saturated with vapor by being forced through the oil by pressure of a rubber bulb from degree to degree, while at the same instant a small flame is brought to the mouth of the oil holder. The apparatus has the recommendation of simplicity of construction and manipulation, and gives, as I have found, concordant results. Considerable care is, however, necessary to prevent spurting and regurgitation of the oil as the air current is suddenly started and interrupted. A continuous air current, Liebermann says, although simplifying the manipulation, raises the flashing point by preventing the accumulation of vapor enough for an explosion.

This statement I am unable to confirm, finding on the contrary that a continuous current of air, *if only rapid enough*, gives results identical with those of the intermittent method.

As result of my experiments I have adopted a modification of Liebermann's apparatus and method. The apparatus is shown in the cut. The cylinder is 2–3 cm. in diameter and 10–12 cm. long. Just within the wooden cork the small tube contracts to a fine orifice; at *d* it is connected by rubber tubing with a source of compressed air—small water blast, hand bellows or gasholder—the flow of which can be controlled by the pinch-cock *e*. Its use is as simple as its construction; *A* is about ⅓ filled with oil, and secured in a clamp at *d* so that it plunges in a water-bath to the level of the oil.[1] Air is now allowed to flow through *dcb*, and *e* adjusted so that about 0.5 cm. foam is maintained on the surface of the oil. From degree to degree the test is made by bringing a small blowpipe flame or a match for an instant to the mouth of *A*. At the flashing point the vapors ignite and the bluish flame runs down to the surface of the oil.



It is noteworthy that a *slow* continuous current of air gives a considerably higher flashing point. The rapid current is effective by bringing the vapor to the mouth of the tube and diluting it sufficiently to form an explosive mixture.

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[1] If plunged deeper than this, the sides of *A* above the level of the oil may become overheated, and, as they are constantly moistened by the foam, the flashing point is, in consequence, lowered. On this account I prefer a water to an air bath.

The results are very satisfactory, and the apparatus so simple that it can be made in ten minutes in any laboratory. Further important advantages are the ease of manipulation and readiness with which it can be thoroughly cleaned.

In all the apparatus suggested by Meyer's principle the determinations are largely independent of size or shape of oil holder, quantity of oil, means of ignition, distance of spark or flame from surface of oil and rapidity of heating, and in the form above described the determination of the flashing point becomes as easy and trustworthy an operation as that of determining the boiling point, while the results have a significance wholly wanting to those obtained by the older methods.

Determinations of Flashing-points.

1. Comparison of Liebermann's method with the above described modification:

	By L.'s method.			By the modification.		
Petroleum *A*	41	40.1	40.1	40	40	39.9
	40.5	40.5	40	40	40.1	40
Petroleum *B*		29			29	29

2. Influence of varying velocity of air-current:

Petroleum *A.*	Very slow,	43
	Slow,	41
	Fast enough to form 0.5 cm. foam	40
	Very much faster,	39.8 39.5 39.5

3. Influence of height of oil in holder:

Petroleum *C.*	Holder	¼	full	38.5
	"	⅓	"	38.3
	"	⅔	"	37.8

All determinations are in centigrade degrees.

SMITH COLLEGE LABORATORY, *Sept.* 4 1882.

FRIEDRICH WÖHLER.

No one but a chemist can appreciate the full significance of the brief message which came to us a month ago without warning—"Wöhler is dead!" What need be added to it? No chemist was better known or more honored than Wöhler, and none ever deserved distinction and honor more than he. His life was made up of a series of brilliant successes, which not only compelled the admiration of the world at large, but directed the thoughts of his fellow workers and led to results of the highest importance to science.

It is impossible in a few words to give a correct account of the work of Wöhler, and to show in what way his life and work have been of such great value to chemistry. Could he himself direct the preparation of this notice, the writer knows that his advice would be, "Keep to the facts." So far as any one phrase can characterize the teachings of Wöhler, that one does it; and though enthusiasm prompts to eulogy, let us rather recall the plain facts of his life, and let them, in the main, speak for themselves.[1]

He was born in the year 1800 at Eschersheim, a village near Frankfort-on-the-Main. From his earliest years the study of Nature appears to have been attractive to him. He took great delight in collecting minerals and in performing chemical and physical experiments. While still a boy he associated with a Dr. Buch of Frankfort, and was aided by this gentleman, who did what he could to encourage in the young student his inclination towards the natural sciences. The first paper which bears the name of Wöhler dates from this period, and is upon the presence of selenium in the iron pyrites from Kraslitz. In 1820 he went to the University of Marburg to study medicine. While there he did not, however, neglect the study of chemistry. He was at that time particularly interested in an investigation on certain cyanogen compounds. In 1821 he went to Heidelberg, and in 1823 he received the degree of Doctor of Medicine. L. Gmelin became interested in him, and it was largely due to Gmelin's influence that Wöhler gave up his intention of practicing medicine and concluded to devote himself entirely to chemistry. For further instruction in his chosen science, Wöhler went to Stockholm to receive instruction from Berzelius, in whose laboratory he continued to work from the fall of 1823 until the middle of the following year. Only a few years since, in a communication entitled "Jugenderinnerungen eines Chemikers," he gave a fascinating account of his journey to Stockholm and his experiences while working with Berzelius. On his return to Germany he was called to teach chemistry in the recently founded municipal trade school (Gewerbschule) at Berlin. He accepted the call, and remained in Berlin until 1832, when he went to Cassel to live. In a short time he was called upon to take part in the direction of the higher trade school at Cassel. He continued to teach and work in Cassel until 1836, when he was appointed professor of chemistry in Göttingen. This office he held at the time of his death, September 23, 1882.

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[1] See Kopp's Geschichte der Chemie, **4**, 440.

In 1825 Wöhler became acquainted with Liebig, and an intimate friendship resulted, which continued until the death of Liebig, a few years ago. Though they lived far apart, they met during the vacations at their homes, or travelled together. Many important investigations were conceived by them as they talked over the problems of chemistry, and many papers appeared under both their names, containing the results of their joint work. Among such papers may be mentioned: "On Cyanic Acid" (1830); "On Mellithic Acid" (1830); "On Sulphotartaric Acid" (1831); "On Oil of Bitter Almonds, Benzoic Acid and Related Compounds" (1832); "On the Formation of Oil of Bitter Almonds from Amygdalin" (1837); and "On Uric Acid" (1837).

Of the papers included in the above list, the two which most attract attention are those "On the Oil of Bitter Almonds" and "On Uric Acid." In the former it was shown for the first time that in analogous carbon compounds there are groups which remain unchanged, though the compounds containing them may, in other respects, undergo a variety of changes. This is the conception of radicles or residues as we use it at the present day. It cannot be denied that this conception has done very much to simplify the study of organic compounds. The full value of the discovery was recognized at once by Berzelius, who, in a letter to the authors of the paper, proposed that they should call their radicle proin or orthrin (the dawn of day), for the reason that the assumption of its existence might be likened to the dawn of a new day in chemistry. The study of this paper should form a part of the work of every advanced student of chemistry. It is a model of all that is desirable in a scientific memoir. The paper on Uric Acid is remarkable for the number of interesting transformation products described in it, and the skill displayed in devising methods for the isolation and purification of the new compounds. Comparatively little has been added to our knowledge of uric acid since the appearance of the paper of Liebig and Wöhler.

It would lead too far to attempt to give a complete list of the papers which have appeared under the name of Wöhler alone. In 1828 he made the remarkable discovery that when an aqueous solution of ammonium cyanate, $CNONH_4$, is evaporated, the salt is completely transformed into urea, which has the same percentage composition. It would be difficult to exaggerate the importance of this discovery. That a substance like urea which up to that time had only been met with as a product of processes which take place in the animal body, should be formed in the laboratory out of inorganic compounds, appeared to chemists then to be little less than a miracle. To-day such facts are among the commonest of chemistry. The many brilliant syntheses of well-known and valuable organic compounds which have been made during the past twenty years are results of this discovery of Wöhler.

In 1823 he published a paper on secretion, in the urine, of substances which are foreign to the animal organism, but which are brought into the body. He discovered the transformation of neutral organic salts into carbonates by the process of assimilation.

In 1832 he investigated the dimorphism of arsenious acid and antimony oxide. In 1841 he made the discovery that dimorphous bodies have different fusing points according as they are in the crystallized or amorphous condition.

Among the more remarkable of his investigations in inorganic chemistry are those on methods for the preparation of potassium (1823); on tungsten compounds (1824); the preparation of aluminium (1827); of glucinum and yttrium (1828). In 1856, working with St. Claire Deville, he discovered crystallized boron.

Analytical methods were improved in many ways, and excellent new methods were introduced by him. Further, he did a great deal for the improvement of the processes of applied chemistry.

With Liebig he was associated in editing the "Annalen der Chemie und Pharmacie," and the "Handwörterbuch der Chemie." He wrote a remarkably useful and popular "Grundriss der Chemie." The part relating to inorganic chemistry appeared first in 1831, and was in use until a few years ago, when Fittig wrote his "Grundriss" on the same plan, a work which supplanted its prototype.

The above will serve to give some idea of the great activity of Wöhler's life and the fruitfulness of his labors. While thus contributing largely by his own work directly to the growth of chemistry, he did perhaps as much in the capacity of teacher. Many of the active chemists of the present day have enjoyed the advantages of Wöhler's instruction, and many can trace their success to the impulse gathered in the laboratory at Göttingen. The hand of the old master appears in investigations carried on to-day by his pupils.

Wöhler's was not a speculative mind. He took very little part in the many important discussions on chemical theories which engaged the attention of such men as Dumas, Gerhardt, Berzelius, and Liebig, during the active period of his life. He preferred to deal with the facts as such: and no one ever dealt with the facts of chemistry more successfully. He had a genius for methods which has never been equalled. The obstacles which had baffled his predecessors were surmounted by him with ease. He was in this respect a truly great man.

Personally, Wöhler was modest and retiring. His life was simple and unostentatious. He had a kindly disposition which endeared him to his students, to which fact many American chemists who were students at Göttingen during the time of Wöhler's activity can cordially testify. In short, it may be said deliberately that Wöhler, as a chemist and as a man, was a fit model for all of us and for those who will come after us. Though he is gone, his methods live in every laboratory. His spirit reigns in many: could it reign in all, the chemical world would be the better for it.

I. R.

REVIEWS AND REPORTS.

Analytical Chemistry.

Determination of the Flashing Point of Petroleum.—Engler and Haas[1] have thoroughly tested the different forms of apparatus now in use for the determination of the flashing point of petroleum, and find that all those are worthless in which the determination is made indirectly by measuring the tension of the vapor; because the tension of the vapor of petroleum and its inflammability stand in no simple relations to one another. Under this head are classed the apparatus of Salleron-Urbain, van der Weyde, Mensel and others. Those testers in which the petroleum is heated in an open vessel were also found to give unreliable results. The Saybolt tester used in the United States is constructed on this principle, and gave results that were too high. Among the large number of petroleum testers in which the oil is heated in closed vessels many were found to be constructed on false principles, and they discarded such instruments as Tagliabue's, Sintenis's pyrometer, and Parrish's naphtometer. They further state that the following principles are to be kept in mind in testing petroleum, or in judging of the efficiency of the testing apparatus:

The quantity of petroleum used in each case must be the same, and for each separate test a fresh portion must be taken. The heating must be uniform and slow, and the heating period should extend over 10°; and those oils whose flashing point is but little above the temperature of the air should be cooled about 10° before heating. The intensity of the ignition flame and its distance from the surface of the oil must be the same in all the tests. If the size of this flame be increased and its distance from the oil be diminished, the flashing point will be lowered. The ignition flame must never be so near the oil as to cause local vaporization, and for this reason its time of action should be reduced to a minimum. And in general the conditions for the formation of combustible gases in the testing apparatus should resemble, as nearly as possible, those which occur in lamps or petroleum stoves.

Victor Meyer's method was found to possess the advantages claimed by its author. It consists in bringing 40 cc. of the oil to be tested into a glass cylinder of 200 cc. capacity. The closed cylinder is immersed in a water-bath until the water is nearly on a level with its upper edge, the bath is then heated to the temperature at which it is desired to test the oil. The cylinder is taken from the bath and shaken violently, opened, and a small gas jet brought to its mouth. The temperature at which the oil takes fire is called by Meyer "the true or absolute flashing point," because it is independent of the shape and dimensions of the vessel, of the quantity of the oil taken, and of the distance of the ignition flame from the surface of the oil. The correctness of Meyer's view has also been shown by the experiments of Hörler.[1]

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[1] Zeitschrift für analytische Chemie, **20**, 1.

Abel's petroleum tester, adopted by parliamentary act in England, and recently by the German government, was also examined by the authors. The apparatus consists of a small cylindrical petroleum holder provided with a thermometer, and an ingenious device by means of which, on opening the lid of the vessel, the flame of a small lamp is introduced into the opening.[2] The oil holder is surrounded by an air-bath, which in turn is enclosed by a water-bath, the object of the arrangement being to ensure a slow heating of the oil. As the temperature of the oil is thus gradually increased, it is only necessary to slide back the lid from time to time and read the thermometer when the vapor takes fire. Engler and Haas obtained concordant results with this apparatus, but regard the values thus found as too low. The same may be said of Bernstein's tester, except that, in this case, the values were too high.

The best results, however, were obtained with instruments made by the authors themselves, and provided with arrangements for exploding the vapor by means of an electric spark. Engler's apparatus is an improved form of Parrish's naphtometer; while Haas has adopted a modification of Victor Meyer's method. Both instruments are complicated, and considerable skill is required in testing with them.

Skalweit[3] has suggested that the specific gravity, the boiling point, and the index of refraction of petroleum be used in judging of its fitness for use. He finds those oils which give off inflammable vapors to have a specific gravity less than .800, while good petroleum is considerably heavier (.824), and, in the same way, the boiling point and the index of refraction increase as the temperature of the flashing point rises.

Engler and Haas[4] have tested a large number of oils in the ways suggested by Skalweit, and arrived at the conclusion that neither the index of refraction, the boiling point, nor the specific gravity can be used as an accurate means of distinguishing between high and low grades of oils.

Recently Liebermann[5] has invented a new petroleum testing apparatus. The principle adopted is a modification of Victor Meyer's, and consists in forcing a current of air through the heated petroleum. The air becomes charged with the petroleum vapor, and is tested from time to time with a lighted match. That temperature of the oil at which the current of air ignites is taken as the flashing point.

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[1] Dingler's polyt. Journal, **234**, 52.

[2] Dingler's polyt. Journal, **245**, 165.

[3] Chemical News, **43**, 77.

[4] Zeitschrift für analytische Chemie, **20**, 362.

[5] Zeitschrift für analytische Chemie, **21**, 1.

Detection and Estimation of Fusel Oil.—Until quite recently we have had no accurate method for the determination of fusel oil in alcohol or brandy. In 1837 Meurer suggested a solution of one part of silver nitrate in nine parts of water as a reagent for its detection, stating that when added to alcohol containing fusel oil a reddish brown color is produced, and in case large quantities are present a dark brown precipitate is formed. It was soon found, however, that other substances than amyl alcohol produce brown colored solutions with silver nitrate; and Bouvier[1] observed that on adding potassium iodide to alcohol containing fusel oil the solution is colored yellow, from the decomposition of the iodide. Subsequently Böttger[2] proved that potassium iodide is not decomposed by pure amyl alcohol, and that the decomposition is due to the presence of acids contained in fusel oil. More accurate results are obtained by using a very dilute solution of potassium permanganate, which is decomposed by amyl alcohol much more rapidly than by ethyl alcohol.

Dupré[3] determines fusel oil by oxidizing a definite quantity of the alcohol in a closed vessel with potassium bichromate and sulphuric acid. After removal of excess of the oxidizing reagents, the organic acids are distilled, and, by repeated fractional distillation, the acetic acid is separated as completely as possible. The remaining acids are saturated with barium hydroxide, and the salts analyzed; a difference between the percentage of barium found and that of barium in barium acetate proves the presence of fusel oil, and the amount of difference gives some idea of its quantity. Betelli[4] dilutes 5 cc. of the alcohol to be tested with 6–7 volumes of water, and adds 15–20 drops of chloroform and shakes thoroughly. If fusel oil is present its odor may be detected by evaporating the chloroform; or, by treatment with sulphuric acid and sodium acetate, the ether is obtained, which can be readily recognized. Jorissen[5] tests for fusel oil by adding 10 drops of colorless aniline and 2–3 drops of hydrochloric acid to 10 cc. of the alcohol. In the presence of fusel oil a red color is produced within a short time, which can be detected when not more than .1 per cent. is present. But Foerster[6] objects to this method because he finds the color to be due to the presence of furfurol, and that pure amyl alcohol gives no color with aniline and hydrochloric acid.

Hager[7] detects fusel oil as follows: If the spirit contains more than 60 per cent. of alcohol it is diluted with an equal volume of water and some glycerine added, pieces of filter paper are then saturated with the liquid and exposed to the air. After the evaporation of the alcohol, the odor of the fusel oil can be readily detected. For the quantitative determination he distills 100 cc. of the alcohol in a flask of 150–200 cc. capacity connected with a condenser, and so arranged that the apparatus does not extend more than 20 cm. above the water-bath. This arrangement prevents the fusel oil from passing over. If the alcohol is stronger than 70 per cent. and the height of the distillation apparatus is not more than 17 cm., the residue in the flask may be weighed as fusel oil. With a weaker alcohol, or an apparatus which projects further out of the water-bath, the residual fusel oil is mixed with water. It can, however, be separated by adding strong alcohol and redistilling, or by treating with ether, which dissolves the amyl alcohol, and distilling, the temperature being raised finally to 60°.

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[1] Zeitschrift f. anal. Chem. **11**, 343.

[2] Dingler's polytech. Journ. **207**, 516.

[3] Pharm. J. Trans. [3] **6**, 867.

[4] Berichte d. deutschen chem. Gesellsch. **8**, 72.

[5] Pharm. Centralhalle **22**, 3.

[6] Berichte d. deutsch. chem. Gesellsch. **15**, 230.

[7] Pharm. Centralhalle **22**, 236.

Marquardt,[1] like Betelli, extracts the fusel oil from alcohol by means of chloroform, and by oxidation converts it into valeric acid. From the quantity of barium valerate found he calculates the amount of amyl alcohol present in the original solution. 150 cc. of the spirit, which has been diluted so as to contain 12–15 per cent. of alcohol, are shaken up thoroughly with 50 cc. of chloroform, the aqueous layer drawn off and shaken with a fresh portion of chloroform. This treatment is repeated several times. The extracts are then united and washed repeatedly with water. The chloroform, which is now free from alcohol and contains all the fusel oil, is treated with a solution of 5 grams of potassium bichromate in 30 grams of water and 2 grams of sulphuric acid, and then heated in a closed flask for six hours on a water-bath at 85°. The contents of the flask are then distilled, the distillate saturated with barium carbonate, and the chloroform distilled; the residue is evaporated to a small volume, the excess of barium carbonate filtered off, and the filtrate evaporated to dryness, and weighed. The residue is dissolved in water, a few drops of nitric acid added, and the solution divided into two portions. In the first portion the barium is determined; in the second the barium chloride. The total per cent. of barium minus that of barium chloride gives the amount present as barium valerate, from which is calculated the per cent. of amyl alcohol. By this process the author has determined one part of fusel oil in ten thousand of alcohol. To detect very minute quantities of fusel oil, the chloroform extracts are treated with several drops of sulphuric acid and enough potassium permanganate to keep the solution red for twenty-four hours. If allowed to stand in a test tube, the odor of valeric aldehyde will first be noticed, then that of amyl valerate, and lastly that of valeric acid.

Pure Grape Sugar and its Estimation with Standard Solutions.—Worm Müller[2] finds that, contrary to the statements of Soxhlet, grape sugar can be crystallized from its solution in absolute alcohol in a perfectly pure and anhydrous condition. Otto[1] states that the most advantageous conditions for its preparation are as follows: 600 cc. of 80 per cent. alcohol, to which 20 cc. of concentrated hydrochloric acid have been added, are treated with cane sugar, from time to time, until in about three or four weeks the solution will have become saturated. It is now filtered into a dry flask through a paper previously moistened with alcohol, and the filtered solution set aside in a cool place to allow the grape sugar to crystallize. In about four or five weeks the separation will be complete; the liquid is then decanted, and 90 per cent. alcohol added to the crystals. After standing twenty-four hours, the mass is stirred up well and the solution filtered with the aid of a pump. The crystals are then pulverized under absolute alcohol, and, after standing some time, are again filtered. This process of purification is repeated until the filtrate gives no acid reaction, and a concentrated solution of the sugar gives no precipitate with nitric acid and silver nitrate. The sugar is then dried, first in a vacuum, then over sulphuric acid, and lastly, before using, it is dried in a water-bath, the temperature of which is gradually raised from 40° to 100°, to avoid the fusion which takes place if the sugar be immediately introduced into the bath at 100°. Prepared in this way the sugar is perfectly pure, and it is unnecessary to recrystallize from absolute alcohol.

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[1] Berichte d. deutsch. chem. Gesellsch. **15**, 1370 and 1663.

[2] Journ. f. prakt. Chem. **26**, 78.

When grape sugar is titrated with Knapp's solution (10 grams $Hg(CN)_2$ and 100 cc. NaOH (sp. gr. 1.145) to the litre), Otto finds it necessary to dilute the latter with from two to three volumes of water, and to add the sugar solution (which should contain less than 1 per cent.) in small quantities (2 cc.) at a time, boiling after each addition. It is only by observing these precautions that he obtained concordant results. The end of the reaction was ascertained by testing a drop of the solution with ammonium sulphide.

Degener[2] ascribes the varying reducing power of Fehling's solution to the easily reducible copper compound which it contains. He dissolves copper tartrate in sodium hydroxide (3 molecules $CuC_4H_4O_6$ to 4NaOH) and adds the usual quantity of sodium potassium tartrate and sodium hydroxide required to make Fehling's solution. Prepared in this way, he regards the copper as being present in a different form from that in Fehling's solution; and states that whenever 3–4 molecules of free alkali and 16–18 molecules of sodium potassium tartrate are present to 3 atoms of copper, the degree of concentration of the solution has no effect upon its reducing power; and that, after boiling, the sugar will have reduced copper in the proportion of six molecules of copper oxide to one of sugar.

E. H. K.

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[1] Journ. f. prakt. Chem. **26**, 87.

[2] Zeitschrift d. Vereins f. Rübenindustrie, 1881, 349.

Carbonic Acid in the Air.

Owing to the varied and important functions of carbonic acid in our atmosphere, the investigation of its amount in the air has always been an attractive problem to chemists. Ever since it has been known that animals produce carbonic acid by respiration, and that plants consume it, appropriating carbon and liberating oxygen, the question has often been asked, Do these two great processes compensate each other perfectly, or is there a tendency towards increase or decrease in the amount of this atmospheric constituent?

The chief causes of production of the gas are:

1. The respiration of animals.
2. Combustion of carbonized material.
3. Exhalations of carbonic acid caused by volcanoes and other intra-terrestrial agencies.

The causes of consumption are chiefly:

1. The decomposition of carbonic acid by plant life.
2. The formation of carbonate of lime by the absorption of atmospheric carbonic acid through the agency of certain animalculae, giving rise to coral reefs and islands and vast limestone deposits.

Owing to insufficient data it cannot be said whether atmospheric carbonic acid is increasing or decreasing; but certainly, if any essential change is going on, such change must be extremely slow, and the most accurate and systematic analyses carried on for years would be necessary to reveal it. From such knowledge as we have, however, the *total* amount of this gas in the atmosphere seems to be constant. In the text-books of to-day we find usually something like the following statement: The atmosphere contains a small amount of carbonic acid, varying usually between 4 and 6 parts by volume per 10,000 of air. Within the last few years a number of investigators have applied themselves in the most painstaking manner to ascertaining what is the correct *mean* proportion of carbonic acid in the air, and what are the limits of variation in the amount of this gas. According as the methods for determining carbonic acid in the air have become more perfect, it is noticeable that the proportion has been found to be less and less, until now, in the light of a number of independent investigations, the analytical processes involved in which were tested and retested until it seems impossible to raise a reasonable doubt as to their reliability, we have as the mean proportion 29.62 parts by volume of carbonic acid to 100,000 of air. For the limits of variation we have the figures 27.00 to about 35.00 parts per 100,000. (These figures are taken from M. Reiset's tables referred to further on.)

A very natural question may now be asked, namely, to what cause or causes is this variation in the proportion of carbonic acid due? *A priori* we would expect to find more carbonic acid in the atmosphere surrounding an abundant source of this gas, for example a large city, than in the atmosphere of the open country, where not only is the production of the gas comparatively small, but where also the decomposing action of vegetation is naturally more active. We would expect to find less carbonic acid in the air surrounding abundant vegetation than in that covering a desert devoid of plant life. Questions to which the answers cannot so readily be anticipated also arise, for example: For a given place is there more or less carbonic acid in the air on a clear day than on a cloudy day? Is there a difference in the proportion between day and night, or between winter and summer? Is there more or less carbonic acid at the bottom of a mountain than at the top? Is there more or less in the air near the sea than in that of inland country? etc.

The number of investigators who have endeavored to solve questions relative to the variation in the proportion of atmospheric carbonic acid is large; few of them, however, have succeeded in furnishing experimental evidence so definite and convincing in character as that submitted to the scientific world by M. J. Reiset[1] in answer to problems of the nature given above. Appreciating the delicate nature of the task before him, M. Reiset's first efforts were directed to securing an analytical method sufficiently accurate to reveal the minutest variations in the small proportion of the gas under consideration. The principle involved in his method is the precipitation of carbonate of barium by passing a known volume of air through a solution of baryta, the strength of which is determined before and after the operation by means of sulphuric acid of known strength. The precautions taken to avoid every imaginable source of error are such as to give entire confidence in the results obtained. The number of determinations made by Reiset is 283, each determination requiring from seven to twelve hours' time for the passage of about 600 litres of air through the absorbing liquid. Some of the determinations lasted twenty-three or twenty-four hours, in order to obtain the mean proportion directly.

The following observations were also made in connection with each analysis:

Hour and minute of beginning, day or night.
Duration of analysis.
Weight of air dry at 0° C. and 760 mm. in the aspirator.
Weight of atmospheric aqueous vapor in air analyzed.
Temperature of the air, and pressure.
Direction of the wind and state of the atmosphere.

By an examination of the tables compiled by M. Reiset the following results are revealed:

1. The maxima in the proportion of carbonic acid always correspond to cloudy, foggy or misty weather.

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[1] Annales de Chimie et de Physique, June, 1882.

2. Air collected during the night contains more carbonic acid than that collected during the day.

3. Minima correspond to days of fine weather, with bright sunlight and absence of clouds.

To determine the influence of vegetation, comparative and simultaneous observations were made at two different stations, one in the midst of abundant plant growth, the other in an open field. The diffusion of the gas in the air is, however, so rapid that variations in its amount due to vegetation are scarcely appreciable. Air analyzed in a fine field of red clover, in the month of June, gave a mean of 28.98 per 100,000; simultaneous observations at the normal station gave in the mean 29.15. The mean of analysis in a rich field of barley was 28.29 per 100,000; that at the normal station 29.33. The following incidental and interesting item was brought out during a single determination: The presence of a flock of three hundred sheep near the apparatus on a certain day of fine weather caused a notable increase in the proportion of carbonic acid; the figures obtained were 31.78 per 100,000. A number of analyses were made near the park Monceau in Paris. During the month of May, when fires begin to be extinguished, the mean was found to be 30.57 per 100,000 of air. The maximum, 35.16, was obtained on the 27th of January, 1879, during the period of most active combustion; the minimum, 29.13, was obtained May 31, 1875. The normal variations in the proportion of carbonic acid are generally between 28 and 30 per 100,000 of air. These variations are more sudden and more numerous during the summer.

Let us now turn our attention to the labors of MM. Müntz and Aubin.[1] These investigators commenced their work with the purpose of solving the three following problems, viz:

1. To determine whether the proportions $\frac{4}{10000}$ and $\frac{6}{10000}$ found by the ealier investigators are not too high as indicated by certain more modern analyses?

2. Does the proportion of carbonic acid in the air vary between wide limits, or is it not practically constant?

3. Is there or not a considerable difference in the proportion for different strata of the atmosphere?

The method employed for the answering of these questions consists briefly in passing a known volume of air through tubes containing pumice-stone saturated with a solution of caustic potash, and, after the operation, in liberating the carbonic acid by means of sulphuric acid and measuring the volume of the gas directly. This process has the following advantage: Tubes may be prepared, filled with the pumice-stone, sealed at both ends, transported to the spot at which the air is to be analyzed, and, after passing the desired amount of air through them, again sealed, returned to the laboratory (after an indefinite time), where the determination of the gas can be made. The delicate part of the operation is thus performed where there are laboratory facilities. Another advantage consists in the rapidity with which the air can safely be passed through these tubes, *i. e.* at the rate of 3 litres per minute. Before adopting this method the authors first tested it thoroughly by operating on air first deprived of carbonic acid and then mixed with a small but known amount of the gas, which was then redetermined; thus in an artificial air containing 3.03 CO_2 per 10,000 air, 2.98 was found. A large number of test experiments were made before the method was finally adopted.

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[1] Annales de Chimie et de Physique, June, 1882.

For the investigation of the lower atmospheric strata Müntz and Aubin established two stations, one at Paris at the Conservatoire des Arts et Métiers, 6m. above the ground, the other in the open plain which extends towards the plateau de Gravelle 4m. above the ground. The mean proportion found for the Paris station is 3.19 parts by volume of carbonic acid to 10,000 of air; the mean for the country station is 2.84. These figures do not differ materially from those given by M. Reiset.

A number of comparative determinations were made at Paris and Joinville. For Paris we have the figures 2.99, 3.06, 2.89, 2.96; for Joinville the figures 2.74, 2.72, 2.85, 2.79. It is thus established that the air of Paris contains more carbonic acid than that of the country.

An examination of the tables submitted by Müntz and Aubin shows that the proportion is at its minimum when the air is disturbed and the sky clear; at its maximum when the weather is cloudy and calm. The absolute minimum is 2.70, the absolute maximum 3.17. These figures confirm those of M. Reiset.

Having thus arrived at solutions of the first two problems, the influence of altitude was investigated. Much discussion has taken place on this point, some observers having found the proportion greater at high than at low altitudes, others greater at low than at high elevations.

The summit of the Pic du Midi, altitude 2877 m., in the Pyrenees was selected for high altitude observations. The mean of fourteen analyses at the summit is 2.86; that for low altitude observations was 2.81; hence the proportion is not sensibly different in the upper strata of the air.

Before closing it will perhaps not be out of place to state certain results arrived at by M. Schloesing,[1] who has a theory that the sea is a great regulator of the proportion of atmospheric carbonic acid. This investigator found that certain neutral carbonates of the alkaline earths placed with water in an atmosphere containing carbonic acid are able to absorb this gas and thus to pass into solution as bicarbonates. The extent of this action is a function of the tension of the gas, and when the tension is sufficiently low the bicarbonates give up carbonic acid and are reprecipitated as neutral carbonates. His theory is then that the sea, by absorbing or emitting carbonic acid according to the tension of the latter in the air, acts as a reservoir or regulator for this atmospheric constituent.

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[1] Comptes Rendus, **90**, 1410.

Want of space only prevents a consideration of the investigations of many other observers whose labors are of interest in connection with the subject. We may now not only consider ourselves as in possession of figures expressing very accurately the general mean proportion of carbonic acid in the air, but also as having some reliable knowledge of causes of local variation.

Another question which might well be asked is this: Is there not some connection between the variations in the proportion of carbonic acid in the air and the great general movements of the latter? This question has been propounded and a solution attempted by M. Marie-Davy, but since the method employed and the analytical results obtained by him have been rather severely criticized, the question must still be considered an open one. Moreover, definite knowledge on this point can be gained only by a long series of simultaneous determinations at places widely separated. For this purpose the method of Müntz and Aubin seems eminently well adapted, since skilled manipulation in connection with it is essential only in the laboratory, where the necessary tubes might be prepared, sent to various stations, and, after passing the necessary amount of air through them, returned to the laboratory for the completion of the analysis. W. C. D.

ON SOME RECENT IMPROVEMENTS IN INDUSTRIAL CHEMICAL PROCESSES.[1]

The improvements in question relate to the manufacture of chlorates, to the manufacture of carbonate of potash, to the recovery of sulphur from alkali waste, and to the industries of sulphuric acid, sulphate of soda, and chlorine.

Commencing with the chlorates, I may remind you that the manufacture of these salts is based on the reactions which take place when milk of lime is treated by an excess of chlorine. Theoretically, the product of the treatment of milk of lime by chlorine should be a mixed solution of one equivalent of calcium chlorate and five equivalents of calcium chloride:

$$6CaO+12Cl=CaCl_2O_6+5CaCl_2.$$

In industrial practice, however, the product always contains appreciably more than five equivalents of calcium chloride. It never contains less than five and a half equivalents, and frequently contains as much as six and a half equivalents, of that salt. Its average composition may be taken to be

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[1] This paper was recently read by Mr. Walter Weldon before the "Society of Chemical Industry," and has appeared in the Journal of the Society.

$$CaCl_2O_6+6CaCl_2.$$

Between calcium chlorate, in solution in water, and potassium chloride, double decomposition takes place; and it is by this double decomposition that chlorate of potash is now invariably manufactured. Continental manufacturers usually treat simply milk of lime by chlorine, and then add potassium chloride to the resulting "crude chlorate liquor," as it is called, whilst English manufacturers usually add their potassium chloride to their milk of lime before commencing the treatment by chlorine; but in both cases equally the final product is a mixed solution of two of potassium chlorate and from six and a half to seven and a half, say on an average seven, of calcium chloride:

$$CaCl_2O_6+6CaCl_2+2KCl=2KClO_3+7CaCl_2.$$

This mixed solution is treated for the separation of potassium chlorate from it by being concentrated to a certain point by evaporation and then allowed to cool, when chlorate of potash crystallizes out. The whole of the potassium chlorate, however, does not crystallize out; from fourteen or fifteen to as much as twenty-five per cent. of it, according to circumstances, remains with the mother-liquor. By further evaporating the mother-liquor, and then again cooling, more chlorate of potash would be obtained; but this further quantity would be so contaminated by calcium chloride, which would crystallize out with it, as to be inapplicable to any of the purposes for which chlorate of potash is at present required. The mother-liquor is therefore usually thrown away. Attempts have from time to time been made to turn it to some small account by treating it by hydrochloric acid, from which the potassium chlorate in it then liberates chlorine; but this operation is attended by a certain amount of danger, and moreover chlorine is now produced so cheaply in other ways that the game is not worth the candle.

In the manufacture of chlorate of potash, then, as at present ordinarily conducted, there is a loss of from fifteen to twenty-five per cent. of the total chlorate produced. The improvement to which I shall first invite your attention enables this loss to be reduced to below five per cent. The improvement in question was devised, however, not for the purpose of thus diminishing the loss in the manufacture of chlorate of potash, but for quite another purpose, and its application to this other purpose may most conveniently be noticed first.

The members present will be aware that, although until comparatively recently, the only chlorate which occurred in commerce in any considerable quantity was the chlorate of potash, within the last few years a demand has sprung up for the very much more soluble salt, chlorate of soda. This demand for chlorate of soda, I may say, in passing, is an outcome of our President, Professor Roscoe's famous researches on vanadium. Some of the rougher furnace work on the raw material from which Professor Roscoe obtained his vanadium was done for him by Mr. Samuel Mellor, of the Magnesium Metal Company, at that company's works at Patricroft, near Manchester. In acknowledgment of it, Professor Roscoe presented to Mr. Mellor some ounces of vanadium salts, and Mr. Mellor sent them to Messrs. Johnson and Matthey, for whom some portions of them were obtained by the late Mr. John Lightfoot, of Accrington, and by Mr. Robert Pinkney, of London. Both these gentlemen experimented with them in connection with their application to the production of aniline black, with the result of finding that they were far more effective for the purpose than the copper salts which had previously been used, while their use instead of copper salts would avoid the inconveniences which had led to the abandonment of the use of aniline black by many firms of calico-printers, that inconvenience being that when using a "color" containing a copper salt, copper deposited on the "doctors," or scrapers. Before knowing of these results, Dr. Roscoe had urged Mr. Mellor to try to find a deposit of vanadium, and to commence the manufacture of vanadium salts, his view being that if compounds possessing such remarkable properties were only rendered accessible to chemists, uses would speedily be found for them. Mr. Mellor acted on this advice, and, after surmounting very great difficulties, was at length enabled to put vanadium salts into the market. To induce calico-printers to use them, however, was no easy task. It took immense labor to convince them that a vanadium salt at twenty-one shillings an ounce could be cheaper for their purpose than copper sulphide at a few pence per pound, which it, however, certainly is, since only one halfpennyworth of the costly vanadium salt is required for each gallon of "color," whereas, when using copper sulphide, the quantity of it required per gallon of "color" costs at least seven halfpence. There was, moreover, a further difficulty. The "color" used for printing aniline black must contain, not only an aniline salt and a metallic salt, but also an oxidizing agent; and the only available oxidizing agent then occurring in commerce was chlorate of potash. But the solubility of chlorate of potash is comparatively so slight that only four ounces of it could be got dissolved in each gallon of "color," and this was insufficient to completely oxidize the aniline, and the blacks produced were therefore apt to turn green. Before aniline black could be largely employed by calico-printers, even now that vanadium salts were at their disposal, it was therefore necessary to provide them with a more soluble oxidizing agent than chlorate of potash; and Mr. Mellor was thus led to undertake the manufacture of chlorate of soda. Some calico-printers had already begun to use chlorate of soda, producing it themselves, in solution, by various double decompositions with chlorate of potash; but Mr. Mellor was the first to produce chlorate of soda in crystals, and to render it readily obtainable by whosoever required it; and it is to his introduction into commerce of that salt, together with vanadium salts, that the great extension which the application of aniline black in calico printing has since undergone is mainly due. Chlorate of soda, so far as I am aware, is at present used only by calico-printers, and only in the printing of aniline black; but some two hundred tons of it are now produced per annum, and its manufacture is still extending.

For some years after a demand for chlorate of soda was thus created by Mr. Mellor, the demand for that salt was met by various methods, all of which had this in common, that previously manufactured chlorate of potash was taken as their starting-point. Of these methods it will be sufficient to mention that which consisted in decomposing chlorate of potash by aqueous hydrofluosilicic acid, thus obtaining silicofluoride of potassium and a solution of chloric acid, and then saturating the latter either by caustic soda or by sodium carbonate.

The reason why such methods as these were resorted to appears to have lain in the very positive statement of the books that sodium chlorate cannot be separated from a mixed solution of sodium chlorate and sodium chloride, by reason of the two salts being of equal solubility. This statement appeared to render hopeless any attempt to manufacture sodium chlorate by means of the otherwise obvious reaction of sodium sulphate on "crude chlorate liquor," since that reaction would yield a mixed solution of sodium chlorate and sodium chloride, containing very much more of the latter salt than of the former:

$$CaCl_2O_6 + 5.5CaCl_2 + 6.5Na_2SO_4 = 2NaClO_3 + 11NaCl + 6.5CaSO_4$$

One chemist, however, declined to accept this statement of the books. My friend, Monsieur Pechiney, of the great chemical works of Salindres, in the south of France, preferred to investigate the solubility of sodium chlorate for himself; and he found that the statement of the books that its solubility is almost exactly the same as that of sodium chloride is true only for certain temperatures. At ordinary temperatures the solubility of sodium chlorate is almost the same as that of sodium chloride; but at higher than ordinary temperatures the respective solubilities of the two salts are widely different. While the solubility of sodium chloride, as we know, does not appreciably increase with increase of temperature, M. Pechiney found, not only that the solubility of sodium chlorate does increase with increase of temperature, but that it increases to such an extent that mere concentration by evaporation of a mixed solution of sodium chlorate and sodium chloride will cause practically the whole of the sodium chloride to fall down, or "salt out," leaving sodium chlorate only in solution.

Having obtained this result, M. Pechiney was enabled some four year ago to commence producing chlorate of soda by the following series of operations:

1. Production of crude chlorate liquor, by acting upon milk of lime by excess of chlorine.
2. Treatment of the crude chlorate liquor by sodium sulphate.
3. Filtration of the product of the second operation by means of the centrifugal hydro-extractor.
4. Evaporation of the filtrate until sodium chloride ceased to fall, the sodium chloride being constantly "fished out" as it fell.
5. Cooling of the solution thus freed from sodium chloride, giving crystals of practically pure chlorate of soda, and a small quantity of mother-liquor consisting of a saturated solution of that salt.

While, however, this method of manufacturing chlorate of soda was a very great advance upon all preceding methods, M. Pechiney was by no means satisfied with it. As is shown by the equation given above, the reaction of sodium sulphate on crude chlorate liquor requires at least six and a half of Na_2SO_4 to give two of $NaClO_3$, and its products are a mixed solution of two of sodium chlorate and at least eleven of sodium chloride, holding in suspension at least six and a half of calcium sulphate. The presence in the product of so much calcium sulphate occasioned considerable loss of sodium chlorate, since it was impossible industrially to separate the calcium sulphate completely from the mixed solution without incurring too much expense for the evaporation of wash-waters; and the presence of so large a proportion of sodium chloride in the mixed solution was a further cause of loss of chlorate, since in fishing out the sodium chloride, during the evaporation of the filtrate from the calcium sulphate, much adherent solution of sodium chlorate was of course necessarily fished out with it. Moreover, water enough had to be used to hold in solution not only the two of sodium chlorate, but also the eleven of sodium chloride; and all this water, or at least all of it not lost as mother-liquor adherent to the solid impurities which had to be separated from the sodium chlorate, as well as the water used for washing the calcium sulphate, had, of course, to be afterwards driven off by evaporation. In a district in which coal is dear this was a serious matter.

Now, it is obvious that eleven-thirteenths of the calcium sulphate and the whole of the sodium chloride contained in the product of the reaction of sodium sulphate on crude chlorate liquor are due to the five and a half equivalents of calcium chloride contained in that liquor. Between calcium chlorate only and sodium sulphate the reaction would be—

$$CaCl_2O_6 + Na_2SO_4 = 2NaClO_3 + CaSO_4.$$

This reaction would yield, instead of a mixed solution of two of sodium chlorate and eleven of sodium chloride, holding in suspension six and a half of calcium sulphate, a solution of two of sodium chlorate with no sodium chloride at all, holding in suspension only one of calcium sulphate. If, therefore, in the manufacture of sodium chlorate, one could start from calcium chlorate exempt from calcium chloride, one would gain some very important advantages. Not only would the consumption of sodium sulphate, per given quantity of sodium chlorate produced, be only two-thirteenths of the quantity required when starting from crude chlorate liquor, while the total quantity of materials to be dealt with, and the quantity of water to be evaporated, would also be less, in about the same proportion, than in the latter case, but the loss of sodium chlorate would be only one-tenth of what it is when starting from crude chlorate liquor, by reason of the amount of foreign bodies to be separated from the sodium chlorate being only one-tenth of the total amount which is present with that salt when it is produced by the reaction of sodium sulphate on calcium chlorate associated with five and a half equivalents of calcium chloride.

These considerations led M. Pechiney to attempt to obtain industrially, under conditions under which it should be available for the production of sodium chlorate from it, if not absolutely pure calcium chlorate, at least a mixture of calcium chlorate and calcium chloride containing a very much smaller proportion of the latter salt than is contained in the crude product of the action of chlorine on milk of lime. It being hopeless to obtain calcium chlorate by any new reaction, M. Pechiney proposed to himself the problem of separating calcium chloride from crude chlorate liquor. For my own part, although perhaps not entirely lacking boldness in such matters, I must say that if this problem had been proposed to me, I should have recoiled before it, and should have regarded its solution as impracticable. M. Pechiney, however, zealously aided by his friend and mine, M. Gladyzc, the very able chemist attached to the works of Salindres, has solved it in a very simple way.

The crude chlorate liquor produced at Salindres contains five and a half equivalents of calcium chloride, and has a density of 25° Beaumé. M. Pechiney now evaporates that liquor until its density while boiling is 48° Beaumé. He then cools the liquor so concentrated to at least 12° C., but not below 10° C. Of its five and a half equivalents of calcium chloride, 4.3 equivalents are thus caused to crystallize out as $CaCl_2.2H_2O$. The concentrated liquor must be cooled to at least 12° C., or this proportion of calcium chloride would not crystallize out; but it must not be cooled below 10° C. or calcium chlorate would crystallize out as well. The crystals obtained between these limits of temperature have no crystallized calcium chlorate with them, and they are of a nature permitting them to be separated from their mother-liquor, by means of the hydro-extractor, so completely, that the loss of chlorate through mother-liquor adherent to them is barely appreciable. The mother-liquor is a solution of 1.0 equivalent of calcium chlorate and 1.2 equivalent of calcium chloride. To this liquor M. Pechiney now adds, first its own volume of water, and then three times 1.2 equivalents of lime. He then heats to at least 80° C., to determine the formation of calcium oxychloride. He then cools to ordinary temperatures, and then again filters by means of the hydro-extractor. The filtrate obtained this time is a solution of one equivalent of calcium chlorate and only three-tenths of an equivalent of calcium chloride, and thus contains less than one-eighteenth of the proportion of calcium chloride which was contained in the crude chlorate-liquor commenced with. The last three-tenths of an equivalent of calcium chloride M. Pechiney has hitherto failed to separate; but the separation of all but that small proportion is now daily performed at Salindres on a very considerable scale.

I ought here to say that the mixture of calcium oxychloride and excess of lime which is separated by the second filtration is much more retentive of mother-liquor than the crystals of hydrated calcium chloride which are separated by the first filtration; but this occasions no loss of chlorate, because M. Pechiney uses the mixture of calcium oxychloride and free lime for the preparation of more chlorate liquor. And in this connection I may mention an interesting point. While the reaction of chlorine upon milk of lime takes place with evolution of heat, the formation of calcium oxychloride, by the combination of calcium chloride with lime, takes place with an absorption of heat, and the quantity of heat absorbed in the one case seems to be just the same as the quantity evolved in the other. Hence, while the action of chlorine on milk of lime causes a rise of temperature, there is no change of temperature at all when calcium oxychloride is treated by chlorine, the heat liberated by the reaction of the chlorine on the lime of the oxychloride being just sufficient to decompose the oxychloride and no more.

At Salindres, then, there is now regularly produced a solution of calcium chlorate having associated with it only three-tenths of an equivalent of calcium chloride instead of the five and a half of chloride per one of chlorate, which are contained in crude chlorate liquor. I will not further dwell upon the obvious economy with which M. Pechiney is thus enabled to manufacture chlorate of soda; but I may here recur for one moment to chlorate of potash. M. Pechiney now uses in the manufacture of this salt also the solution obtained by separating calcium chloride from crude chlorate liquor, in the manner I have indicated, and he is thus enabled to obtain his potassium chlorate associated with so much less calcium chloride than formerly, that he can regularly crystallize out from his solutions of the two salts fully ninety-five per cent. of the potassium chlorate contained in them, in place of the seventy-five per cent. only, which is all that it is possible to crystallize out in the climate of Salindres from the mixed solution of those two salts produced in the ordinary way.

While by realizing a practical method of separating calcium chloride from calcium chlorate, as contained in crude chlorate liquor, M. Pechiney is able, as we have seen, to effect a very considerable economy in the manufacture of chlorate of soda, and a large, though not equally large, economy in the manufacture of chlorate of potash, the event will probably show that he has done very much more than this. There is every probability that his new product—1.0 of calcium chlorate and 0.3 of calcium chloride—will itself become an article of commerce, and will be largely applied in the arts to other purposes than those to which M. Pechiney himself applies it. Solution of pure calcium chlorate, treated by sulphuric acid, would of course give a solution of chloric acid; while a solution of 1.0 of calcium chlorate and 0.3 of calcium chloride, similarly treated by sulphuric acid, gives a mixed solution of chloric acid and of the products of the reaction of chloric and hydrochloric acids upon each other. Such a solution attacks many organic bodies with remarkable energy, and already promises to give results, in connection with the manufacture of organic coloring matters, of very exceptional interest and importance. I have no doubt, for my own part, that calcium chlorate, now for the first time placed in the hands of the industrial chemist, will be found by him an instrument of extreme utility.

I will next touch very briefly upon two other processes which M. Pechiney has recently introduced into his own works, although they are processes of only limited applicability. One of them is a process for recovering sulphur from soda waste. The works of Salindres are situated in the midst of vineyards, or what were such before the days of the phylloxera, and they are no exception to the rule that in the neighborhood of all inland soda-works vast quantities of "tank-waste" accumulate. From heaps of tank-waste exposed to atmospheric influences, there constantly runs, as we know, little rivulets of "yellow liquor," consisting essentially of a mixed solution of calcium sulphydrate and calcium bisulphide. It is believed by many that such a solution would be a capital thing for vineyards afflicted with phylloxera; but the farmers in M. Pechiney's neighborhood preferred to regard it as an excuse for getting M. Pechiney to pay them damages. In all countries to which my experience extends, I have noticed that farmers have a tendency to prefer to exploit any chemical work in their neighborhood rather than to exploit their land. To get rid of all annoyance from this cause, it was necessary for M. Pechiney to treat his yellow liquor for the recovery of sulphur from it; and he has for some time done this by a process somewhat simpler than any in use elsewhere. He simply injects air into the yellow liquor, by means of a Körting's injector, and then, when oxidation has just reached the point at which treatment of the product by an acid would not cause evolution of either H_2S or SO_2, he decomposes the product by hydrochloric acid. Apart from its simplicity, and its requiring so little labor and plant, the chief point of interest about this process is that during the operation of oxidising the yellow liquor there occurs a considerable precipitation of lime. The lime is precipitated in a peculiarly dense state (I exhibit a sample of it), permitting it to be separated from the mother-liquor very readily and completely. Owing to this separation of lime during the operation of oxidising the mother-liquor, the quantity of hydrochloric acid required for the decomposition of the oxidised product is very appreciably less, per given quantity of sulphur obtained, than in any other process for obtaining sulphur from alkali waste, excepting one which I shall have to refer to further on, which is at present only in the experimental stage, but which is likely, I think, to come into general use, and in which no acid will be used at all. This precipitation of lime, and of lime only, is of course due to a part of the calcium sulphide, or of one or more of the calcium sulphides, present in the yellow liquor, giving up sulphur in exchange for oxygen, the sulphur thus replaced going to raise the remainder, or some part of the remainder, of the sulphide or sulphides present, to some higher state of sulphurisation.

The company which owns the works of Salindres also owns the great salt-work of Giraud, in that one of the deltas of the Rhone which is known as Camargue. It was at Giraud that was worked out by my friend, the late Henri Merle, the founder both of Giraud and of Salindres, the process, suggested by the late Professor Balard, the discoverer of bromine, for separating potassium chloride and magnesium sulphate from the mother-liquor left after sodium chloride has crystallized out from salt water concentrated by natural evaporation. This process is practiced on a very large scale at Giraud, and at a certain stage of it there is obtained a mixed solution of sodium chloride and magnesium sulphate. This mixed solution is submitted to artificial refrigeration, by means of Carré's machine, when double decomposition takes place, producing crystallized sodium sulphate and solution of magnesium chloride, which are then separated from each other by means of the hydro-extractor. The sodium sulphate so obtained has associated with it ten atoms of water. Coal at Giraud is very dear; and even where coal is cheap the dehydration of hydrated sodium sulphate, by heating it in furnaces, is a somewhat troublesome operation. M. Pechiney was therefore led to seek some better means of dehydrating the vast quantities of hydrated sodium sulphate produced at Giraud, and the method which he finally arrived at, and now uses exclusively, is as follows: He first adds to the hydrated sodium sulphate a certain proportion of "sel mixte," the product so called being the mixture of sodium chloride and magnesium sulphate which is deposited during the concentration of the mother-liquor, by sun-heat, to 35°B., the degree of concentration at which it begins to deposit double chloride of magnesium and potassium. He then charges the mixture so formed into iron cylinders, furnished with steam coils, by means of which the contents of the cylinders can be rapidly heated. When the contents of the cylinders have attained a temperature of about 35°C.—though M. Pechiney really heats to from 70°C. to 80°C., in order that cooling to below 35°C. shall not take place in the succeeding operation —the contents of the cylinders are found to have become a mixture of anhydrous sodium sulphate with a saturated solution of "sel mixte." The "sel mixte" has dissolved in what was the water of hydration of the sodium sulphate, and all the latter has become anhydrous. The anhydrous sulphate is then separated from the solution of "sel mixte" by means of the hydro-extractor. The whole process is performed in a few minutes, and its only cost is for a very small amount of labor and steam. The anhydrous sulphate obtained is the full quantity corresponding to the hydrated sulphate treated, and it is almost chemically pure. The solution filtered from it is employed for the production of more hydrated sulphate.

(*To be continued.*)

CHEMICAL NOMENCLATURE.

With the desire to aid, as far as possible, in securing uniformity in chemical nomenclature, the simple and excellent rules proposed for this purpose by Dr. Henry Watts, the editor of the Journal of the (London) Chemical Society, are here reprinted. It is to be hoped that American writers on chemical subjects will accustom themselves to observe the rules, unless there are good reasons for deviating from them. What *good* reasons can be given it is difficult to see, unless the fact that one has always used some other less desirable expressions than those proposed be regarded as a good reason.

Rules.

"1. Employ names such as *sodium chloride*, *potassium sulphate*, *ethyl acetate*, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle, *e. g.*, *mercurous* and *mercuric chloride*, *sulphurous* and *sulphuric acid.*

"2. Term compounds of metallic and alcoholic radicles with (OH), *hydroxides* and not hydrates, *e. g.*, potassium hydroxide, phenyl hydroxide, the name hydrate being reserved for compounds supposed to contain water of combination or crystallization. Compounds such as CH_3ONa, C_2H_5ONa, $C_7H_{15}ONa$, etc., should be termed sodium methoxide, ethoxide, heptyloxide, etc.

"3. Apply the term *acid* only to compounds of hydrogen with negative radicles, such as HNO_3, H_2SO_4, H_3PO_4, and denote the oxides which form acids by names such as sulphuric anhydride or sulphur trioxide. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as hydrogen-sodium sulphate, hydrogen-disodium phosphate, etc., to the acid salts. Basic salts are as a rule best designated merely by their *formulæ.*

"4. Use names such as *methane*, *ethane*, etc., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3.(CH_2)_5.CH_3$. The isomeric hydrocarbons are usually most conveniently represented by names indicating their relation to methane: for example, $CH_3.CH_2.CH_2.CH_3$ = propylmethane; $CH_3.CH(CH_3)_2$ = isopropylmethane or trimethylmethane; or, although less frequently, by names such as diisopropyl.

"5. Term the hydrocarbons C_2H_4 and C_2H_2 *ethylene* and *acetylene* respectively (not ethene and ethine). Distinguish the homologues of ethylene, whenever possible, by names indicating their relation to it, such as methylethylene, dimethylethylene, etc., denoting the di-derivatives of the form $C_nH_{2n+1}.HC:CH.C_nH_{2n+2}$ as α-, and those of the form $CH_2:C(C_nH_{2n+1})_2$ as β-compounds: thus $CH_3.CH:CH.CH_3 = \alpha$-dimethylethylene; $CH_2:C(CH_3)_2 = \beta$-dimethylethylene. Similarly, use names such as methylacetylene and dimethylacetylene for the homologues of acetylene of the form $CH \vdots C.C_nH_{2n+1}$ and $C_nH_{2n+1}.C \vdots C.C_nH_{2n+1}$. Adopt the name *allene* for the hydrocarbon $CH_2:C:CH_2$, and indicate the relation which its homologues bear to it in the same manner as pointed out for acetylene.

"6. Distinguish all alcohols, *i. e.*, hydroxyl-derivatives of hydrocarbons, by names ending in *ol*, *e. g.* quinol, catechol, resorcinol, saligenol, glycerol, erythrol, mannitol, instead of hydroquinone, pyrocatechin, resorcin, saligenin, glycerin, erythrite, mannite. Compounds which are not alcohols, but which are at present distinguished by names ending in *ol*, may be represented by names ending in *ole*, if a systematic name cannot be given. For example, write indole instead of indol; furfuraldehyde instead of furfurol; fucusaldehyde instead of fucusol. Ethers derived from phenols, such as $C_6H_5.OCH_3$, etc., hitherto called anisol, anethol, etc., may be distinguished by names ending in *oïl*, as anisoïl and anethoïl.

"Alcohols should be spoken of as mono-, di-, tri-, or n-*hydric*, according to the number of OH groups.

"7. Bodies such as the acids of the lactic series containing the group (OH) should be termed *hydroxy*-, and not oxy-derivatives, *e. g.* hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups C_2H_5O, C_6H_5O, $CH_3.COO$, etc., should in like manner be termed ethoxy-, phenoxy-, acetoxy-derivatives. Thus, ethoxypropionic acid instead of ethyl-lactic acid; 3 : 4 diethoxybenzoic acid instead of diethylprotocatechuic acid; and acetoxypropionic acid instead of acetyllactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6H(C_2H_5)_2(OH)_2.COOH$, and not $C_6H_3(OC_2H_5)_2.COOH$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2.COOH$.

"8. The term *ether* should be restricted to the oxides of hydrocarbon radicles, and the so-called compound ethers should be represented by names similar to those given to the analogously constituted metallic salts (comp. 1).

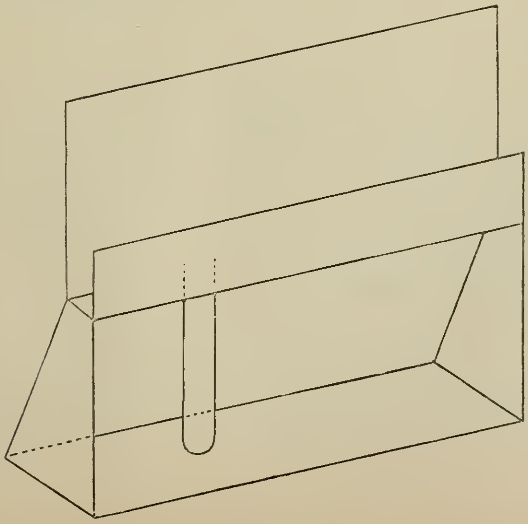
"9. Compounds of the radicle SO_3H should, whenever possible, be termed *sulphonic* acids, or, failing this, *sulpho-compounds:* as benzenesulphonic acid, sulphobenzoic acid, and not sulfi-compounds. Compounds of the radicle $SO_2.NH_2$ should be termed sulphonamides.

"10. Basic substances should invariably be indicated by names ending in *ine*, as aniline, instead of anilin, the termination *in* being restricted to certain neutral compounds, viz. glycerides, glucosides, bitter principles, and proteids, *e. g.* palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen, chloride, bromide or iodide, should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate."

NOTES.

Note on a Tube-Stand for Nesslerizing.

A short time since, while making some determinations by Wanklyn's method of water analysis, we were much troubled by cross-lights, which made it impossible to obtain satisfactory readings. After several attempts we hit upon the following form of stand, which has given the most excellent results, and which has the advantage of being easily and cheaply made. The following figure represents the apparatus.



The tall shield consists of a piece of quarter-inch board six inches wide tacked to the cross-piece. The low shield is three inches wide. The stand and shield are painted black. Over the bottom piece a strip of ordinary window glass, painted white on the under side, is laid. Instead of painting, which of course must be done with a pigment not affected by the laboratory fumes, a piece of white paper may be inserted between the glass and the wood, or the wood itself may be given a coat of white paint. The latter method is in some respects the most advisable, for there is then no danger of breaking the tubes by dropping on the glass. Another advantage is that the wood may receive slight hollows so as to steady the tubes and hold them perpendicular. The whole stand can also be easily made from sheet-iron.

The tubes are ordinary 7-inch test-tubes holding about 60 cc. They project about an inch and a half above the level of the perforated cross-piece. When filled the liquid is about level with the surface of the cross-piece. We find it convenient to mark the number of tenths of ammonia represented by the standard tube on the upright shield behind it. The standard tubes are placed in every other hole, the intermediate holes being used for the tubes containing the distillates. We are in the habit of using two stands each containing twenty holes and ten standard tubes, the two running from 0.01 to 0.20. The tube containing the distillate, after being treated with the Nessler solution, is placed between the two standard tubes to the color of which it approximates the most nearly, and the reading then made.

The stand is placed with the tall upright toward the light. On looking down into the tube, the color appears with remarkable clearness and brilliancy, thus rendering the reading very accurate and satisfactory.

P. T. AUSTEN AND F. A. WILBUR.

NEW BRUNSWICK, N. J.

On Silicon.

It is known that platinum heated in a forge fire, in contact with carbon, becomes fusible. Boussingault has shown that this is due to the formation of a silicide of platinum by means of the reduction of the silica of the carbon by the metal. MM. P. SCHÜTZENBERGER and A. COLSON have produced the same phenomenon by heating to white heat a slip of platinum in the centre of a thick layer of lamp-black free from silica.

The increase in weight of the metal and the augmentation of its fusibility were found to be due, in this case also, to a combination with silicon. As the silicon could not come directly from the carbon which surrounded the platinum, MM. Schützenberger and Colson have endeavored to discover under what form it could pass from the walls of the crucible through a layer of lamp-black several centimetres in thickness, in spite of a volatility amounting to almost nothing under the conditions of the experiment. They describe the following experiments as serving to throw some light upon the question:

1. A thin slip of platinum rolled in a spiral is placed in a small crucible of retort carbon closed by a turned cover of the same material. This is placed in a second larger crucible of refractory clay, and the intervening space filled with lamp-black tightly packed. The whole is then heated to white heat for an hour and a half in a good wind furnace. After cooling the platinum is generally found to have been fused into a button with a marked increase in weight due to taking up silicon, which has penetrated in the form of vapor through the walls of the interior crucible.

2. If in the preceding experiment the lamp-black be replaced by a mixture of lamp-black and rutile in fine powder, the slip of platinum remains absolutely intact and does not change in weight. Thus the titaniferous packing recommended by Sainte-Claire Deville for preventing the access of nitrogen in experiments at high temperatures also prevents the passage of silicon. A mixture of carbon and finely divided iron is on the contrary ineffectual. These facts seem to indicate that nitrogen plays a part in the transportation of the silicon, as this is only prevented by the same means made use of in order to prevent the passage of nitrogen.

3. The volatility of free silicon at a high temperature is too slight to account for the alteration of the platinum at a distance. This can be shown by placing several decigrams of crystallized silicon on the bottom of a small crucible of retort carbon, covering the silicon with a small flat disk of retort carbon upon which is placed the slip of platinum. The crucible closed by its turned cover is then enveloped in a titaniferous packing and kept at a brilliant white heat for an hour and a half. The metal is found to have only very slightly increased in weight, and its properties remain unaltered. This experiment was repeated several times with the same result. If, however, the crystallized silicon be replaced by powdered calcined silica, the platinum, placed upon the carbon disk, fuses and increases in weight, while the silica loses weight. The theory of these curious phenomena is very difficult to establish on account of the high temperatures which are necessary for their manifestation, but it may be concluded, at present, that nitrogen and probably oxygen also play some part in the transportation of the silicon across the intervening space, and that the carbosilicious compounds recently described by MM. Schützenberger and Colson also take part in the phenomenon.—(*Comptes rendus*, **94**, 1710.) R. D. C.

On the Pretended Compound NH_2.

In a recently published article,[1] E. J. Maumené studies the action of potassium permanganate upon ammonium oxalate, by which he professes to have obtained a new compound, to which he gives the formula NH_2. Inasmuch as the existence of a compound NH_2 or rather N_2H_4 (hydrazine) is in no way improbable from a theoretical point of view, seeing that the ethyl and phenyl derivatives of hydrazine are known, it appeared interesting to M. COMBES to repeat the experiments of M. Maumené, which he did with the following results:

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[1] Comptes Rendus, **94**, 571.

1. The carbonate described by Maumené, when treated with hydrochloric acid, gives with platinum chloride a precipitate, the appearance and crystalline form of which are exactly similar to ammonium platinochloride. The analysis of the precipitate shows that it contains from 1.90 per cent. to 1.96 per cent. of hydrogen, while ammonium platinochloride contains 1.80 per cent., and the compound of Maumené only 1.35 per cent.

2. The aqueous solution of the so-called NH_2, neutralized with hydrochloric acid and evaporated to dryness, gives crystals which are absolutely identical with those of ammonium chloride; fractional crystallization always gives the same result. The analysis of this chloride gives from 7.35 per cent. to 7.52 per cent. for its content of hydrogen; ammonium chloride contains 7.47, and the chloride of NH_2 should contain only 5.71 per cent. The only products, then, of the reaction described by M. Maumené are ammonia and carbonic acid.—(*Comptes rendus*, 94, 1717). R. D. C.

Artificial Production of Witherite, Strontianite and Calcite.

L. BOURGEOIS has found that the carbonates of barium, strontium and calcium can be easily crystallized under the ordinary pressure in a bath of certain fused materials. That which has given the best results consists of a mixture of equal equivalents of the chlorides of sodium and potassium. This mixture fuses at dark red heat, and if a few decigrams of precipitated carbonate of barium, strontium or calcium be added to the fused mass, the salt is seen to sink to the bottom of the crucible without the least effervescence. After a few minutes the fused mass is allowed to cool, and the chlorides of sodium and potassium dissolved by washing with water, when there are obtained fine crystals of carbonate of barium, strontium or calcium, identical in their chemical composition and physical properties with the natural mineral species. The carbonate of barium is generally found in hexagonal plates, which under a microscope exhibit faint polarization colors. The carbonate of strontium has only been found in the form of elongated prisms with very marked double refraction, and the carbonate of calcium constantly presents an assemblage of crystals resembling those of snow. When placed under a microscope these hexagonal stars appear colored, and if convergent light be applied they show a black cross completely surrounded by circular rings. —(*Comptes rendus*, 94, 991.) R. D. C.

On two new Antiseptics: the Glyceroborates of Calcium and of Sodium.

G. Le Bon calls attention to two new powerful antiseptic agents, the glyceroborates of calcium and of sodium. The first is prepared by mixing equal parts of borate of calcium and glycerine, and heating the mixture to about 160° with constant stirring; the operation is prolonged until a drop of the mixture allowed to fall from the end of the stirring rod upon a glass plate solidifies on cooling to a clear colorless brittle bead. The hot liquid is then poured out upon a metallic plate and allowed to cool, when it assumes the form of a transparent mass, like glass, which is easily broken up; the fragments while still warm are rapidly introduced into a well stoppered, perfectly dry bottle. The glyceroborate of sodium is prepared in the same manner, simply replacing the borate of calcium by borate of sodium; if, however, fused or anhydrous borate of sodium be used, the proper proportions are 150 parts of glycerine to 100 parts of borax. These two compounds have analogous properties; they fuse at about 150° and are very hygroscopic; exposed to the air they rapidly become liquid, taking up their weight of water. A given quantity of water or alcohol can, however, dissolve twice its weight of glyceroborate. Even in dilute solutions the glyceroborates of calcium and sodium are very powerful antiseptic agents, and present the advantages over phenol of being readily soluble in water in all proportions, entirely without odor, and, above all, in no way poisonous. From a therapeutic point of view the sodium salt seems to be somewhat preferable to the glyceroborate of calcium. Concentrated solutions may be applied to organs as sensitive as the eye without inconvenience. The glyceroborates have also been made use of with entire success to preserve meat during a long voyage.—(*Comptes rendus*, 95, 145.)

R. D. C.

The Luminous Incomplete Combustion of Ether and other Organic Bodies.

The author's attention was called to this subject by observing a pale blue flame floating above the hot sand of a sand-bath when evaporating some ether in the dark. He mentions that the phenomenon has previously been observed by Davy, Doebereiner, and others. Further investigation showed that ether vapor begins to burn with this blue flame at 260°. The experiment may be adapted for lecture illustration by dropping ether on an iron plate heated very nearly to redness; or better, by suspending a hot iron or copper ball over a dish containing filter papers drenched with ether. The temperature of this flame is such that the hand can be held in it with impunity. It will not char paper or ignite carbon disulphide. In large quantities it soon changes into ordinary combustion.

An experiment to determine the products of this incomplete combustion was made by aspirating air saturated with ether vapor through a combustion tube heated by a Bunsen burner, and collecting the volatile products in a test-tube surrounded by a freezing mixture, and absorbing the carbon dioxide by potash bulbs. On examining the aspirated air it was found to be nearly pure nitrogen, the oxygen being used up in the combustion, but the potash bulbs showed that only a very small quantity of carbon dioxide had been formed. For 1.313 gram of oxygen used, only 0.133 gram of carbon dioxide was formed. The products condensed in the test tube were principally aldehyde, ether, and apparently a little crotonic aldehyde. Other substances were experimented with and found to give this flame, but none so well as ether; acetic aldehyde being the next best. The alcohols up to amylic, the hydrides, and the fatty acids, except the two lower members of the series, give it with more or less distinctness. It could not be obtained from any member of the aromatic series. The products of the imcomplete combustion of paraffin were found to be similar to those of ether. The author attributes the luminous appearance to phosphorescence. The light is too feeble to be examined in detail with the spectroscope, but no bands were seen.—(W. H. PERKIN in *Journal Chemical Society*, 1882, 363). J. R. D.

The Determination of Nitric Acid in Soils by Schloesing's Method.

This subject is discussed by R. WARINGTON in two papers: the first being taken up with a description of the precautions necessary in Schloesing's method, and the second in directions for collecting samples of soils and extracting the nitrates, and in a comparison of Schloesing's with the Crum-Frankland and indigo methods. The essential condition necessary to the success of this method is the entire absence of oxygen from the retort in which the reaction takes place. This is obtained by replacing the air with a stream of pure carbon dioxide, and by boiling all the reagents, including those used in the production of the carbon dioxide, immediately before using. The operation is carried on in a small tubulated retort, the bulb of which is about 1¾ inch in diameter. This is heated in a chloride of calcium bath.

The air being entirely expelled from the apparatus by a stream of carbon dioxide, and this gas partly removed by boiling a little water in the retort, the soil extract, concentrated to a very small volume, and mixed with one cc. each of hydrochloric acid and a saturated solution of ferrous chloride, is admitted through a funnel tube, and washed in with very small quantities of hydrochloric acid. The chloride of calcium bath is kept at from 130°–140° until the contents of the retort are evaporated to dryness, and then carbon dioxide is again admitted to expel all the nitric oxide. The gas is collected over mercury, and measured by noting the difference after absorbing the carbon dioxide by potash, and after absorbing the nitric oxide by oxygen. The oxygen should be admitted in only very small excess. The apparatus may be used continuously for several experiments. There is given a series of twelve determinations by this method of nitric oxide in a standard solution of nitre, in which the amounts varied from 5 to 0.5 mg. The quantities found varied from 96.7 to 100.8 per cent. of the quantities taken, the average being 98.4 per cent.

For the collection of samples of soils, the author prefers an iron tube about 9 inches deep and not less than 6 inches square. This is driven into the earth, and the soil filling the tube cut out. It is advisable to take several samples from successive depths, but when only one can be taken it should be from the surface in dry weather. Considerable care is necessary in drying the samples, for if this be done at a temperature of from 90° to 100°, a large proportion of the nitrates is deoxidized by the organic matter and lost, while if the temperature be too low, fermentation goes on and increases the quantity of nitrates. By a number of experiments it was found that the best plan was to place the freshly collected samples in trays in layers an inch thick, and to expose these to a heat of 55° for about 24 hours. After drying, stones and roots are removed and the soil placed in bottles.

The nitrates are extracted by percolation on a filter pump. From 200 to 500 grams of soil are placed on the filter and 100 cc. of water slowly added. The operation is complete in from 10 to 45 minutes, according to the nature of the soil. Experiment showed that second extracts contained no nitrates.

A series of determinations by the Crum-Frankland method, of the nitric oxide in soil extracts free from nitrates, to which a measured volume of a standard solution of nitre was added, seems to show that the organic matter interferes with the reaction. The results are not at all uniform, a few being too high, but the most of them too low, especially when small quantities were used. It is found that nitric oxide is not the only gas given off in the reaction. A similar, but shorter series made by Schloesing's method gives more uniform results. The determinations by the indigo method give only from 64.1 to 76.3 per cent.

The author concludes that Schloesing's method properly carried out is by far the best method for the determination of nitrates in presence of organic matter.—(*Journal Chemical Society*, 1882, 345).

J. R. D.

The Elementary Composition of Starch.

Although the text-books usually give $C_6H_{10}O_5$ or $(C_6H_{10}O_5)_4$ as the established formula of starch, the subject has by no means been positively settled. W. Nägeli[1] concluded from his study of the dextrins that starch has the formula $C_{36}H_{62}O_{31}$, *i. e.* $(C_6H_{10}O_5)_6H_2O$. Later Sachsse[1] decided upon the same formula, while recently Pfeiffer and Tollens[2] have shown with some probability that it is $C_{24}H_{40}O_{20}$ or $C_{24}H_{42}O_{21}$, without being able to decide between these formulas.

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[1] Beiträge zur Kenntniss der Stärkegruppe. Leipzig, 1874.

Elementary analysis has not given satisfactory results, partly, at least, because of the great hygroscopicity of the anhydrous substance. Sachsse converted a weighed quantity of starch into dextrose by boiling with an acid, and determined the dextrose. If the decomposition takes place according to the equation $C_6H_{10}O_5+H_2O=C_6H_{12}O_6$, then one part of starch should give 1.1111 parts dextrose. If, however, the reaction is expressed by $C_{36}H_{62}O_{31}+5H_2O=6C_6H_{12}O_6$, then one part starch should give 1.0909 parts dextrose. The possibility of determining the percentage composition of starch by this method depends, 1st, upon the possibility of converting all the starch into dextrose without the formation of secondary products; 2d, upon the possibility of accurately determining the dextrose thus formed. Each of these steps presents considerable difficulty. The saccharification was successfully accomplished by Sachsse, but his method of determining dextrose was faulty, and hence his conclusions were unreliable.

SALOMON has attempted to solve the problem by the same method, but using for the determination of dextrose Allilin's method[3] as well as determination of the optical rotation and of the specific gravity of the solutions obtained. The values obtained in numerous experiments varied from 1.106 to 1.1131 parts dextrose from 1 part starch; whence, as shown above, the formula of starch must be $(C_6H_{10}O_5)_4$. Pfeiffer and Tollens[4] obtained a compound of the formula $C_{24}H_{39}O_{20}K$ or $C_{24}H_{41}O_{21}K$, or for starch $C_{24}H_{40}O_{20}$ or $C_{24}H_{42}O_{21}$. Analysis failed to decide between these, but showed that starch contains 24 atoms of carbon in the molecule, or a multiple of this quantity. Combining their result with that of Salomon we have as the most probable formula of starch, $C_{24}H_{40}O_{20}$.—(*Journal für praktische Chemie*, [2] **25**, 348.) H. N. S.

Tellurium Sulphur Trioxide.

A century ago Müller von Reichenstein observed that tellurium dissolves in strong sulphuric acid, imparting to it an amethyst-red color. Klaproth[5] observed that this color disappeared on dilution with water, the tellurium being precipitated. From this fact Magnus[6] concluded that the color was due to solution of free tellurium, while Fischer[7] maintained the existence of a definite compound, calling attention to the difference of color between tellurium and its solution, and to the fact that on dilution with water some of it remains in solution as oxide. The question has since been occasionally discussed, but without result. Similar phenomena were observed when sulphur and selenium are dissolved in fuming sulphuric acid, the former giving a blue, the latter a green color. RUDOLPH WEBER[1] obtained bodies of the composition S_2O_3 and $SeSO_3$, by the action of sulphur and selenium on sulphur trioxide, and showed that the blue and green color of the acid is due to solution of these bodies. He now describes an analogous compound $TeSO_3$, which is thus prepared: Finely powdered and carefully dried tellurium is brought in small portions into perfectly anhydrous sulphur trioxide, which is kept at the temperature of 30°–35°. The tellurium changes at once into a red viscous mass, while the trioxide, if pure, remains colorless. The excess of trioxide is then poured off, and that still adhering very carefully evaporated. Thus obtained, the substance is a red amorphous mass, viscous at ordinary temperatures, and transparent only in thin layers, when it shows the amethyst-red color. It soon decomposes at common temperatures, even in close vessels, becoming black with precipitated tellurium and evolving sulphur dioxide. When warmed it is decomposed into Te, TeO_2, SO_2 and some SO_3. It is also instantly decomposed by water, yielding the same products. It is insoluble in perfectly anhydrous sulphur trioxide, but dissolves in common or fuming sulphuric acid, with amethyst-red color. The mean of six analyses gave Te 61.13 per cent. (from 60.40 to 61.81 per cent.) Calculated for $TeSO_3$, Te 61.54 per cent. It is hence analogous to S_2O_3 and $SeSO_3$, which it resembles in chemical and physical properties.—(*Journal für praktische Chemie*, [2] **25**, 218.) H. N. S.

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[1] Chemisches Centralblatt, 1877, 732.

[2] Annalen der Chemie, **210**, 294.

[3] Journal für praktische Chemie, [2] **22**, 22.

[4] Annalen der Chemie, **210**, 29.

[5] Crelle's Annalen, **1**, 98, 1798.

[6] Poggendorff's Annalen, **10**, 492; **14**, 328.

[7] Poggendorff's Annalen, **12**, 153.

Preparation of Mustard Oils.

A. W. HOFMANN states that the mustard oils are best prepared from the disubstituted sulpho-ureas by treating them with a concentrated aqueous solution of phosphoric acid. The sulpho-ureas are easily obtained by treating carbon bisulphide with the amines. Starting with carbon bisulphide and aniline we get diphenyl-sulpho-urea, $CS(C_6H_5)H_2N$; and when this is treated with phosphoric acid it breaks up directly into aniline and phenyl-mustard oil, thus:

$$CS(C_6H_5)_2H_2N_2 = C_6H_5(NH_2) + \underset{\text{Mustard Oil.}}{C_6H_5NCS},$$

—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 985.)

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[1] Poggendorff's Annalen, **156**, 531.

Preparation and Basicity of Hyponitrous Acid.

Hyponitrous acid has hitherto been obtained by treating a nitrate or nitrite with sodium amalgam, or by the electrolysis of sodium nitrate or nitrite, mercury being used as the negative electrode. W. ZORN now finds that it may be readily obtained by treating sodium nitrite with ferrous hydroxide. Milk of lime is added to ferrous sulphate, and to the mixture of ferrous hydroxide and gypsum thus formed is added a solution of sodium nitrite (1 part nitrite to 10 parts ferrous sulphate). The reaction is complete in a few hours. The mass is strained and pressed, and then carefully neutralized with acetic acid. On adding silver nitrate, a precipitate of pure silver hyponitrite (commonly called nitrosyl silver) is formed. The author asserts that Menke's statement that sodium hyponitrite is formed by fusing sodium nitrate with iron filings is not correct, and that Menke must have had either carbonate or phosphate of sodium. When silver hyponitrite is treated with ethyl iodide, a substance of the formula $C_2H_5{-}N_2O_2{-}C_2H_5$ is formed. This appears to be an ester of hyponitrous acid, although its reactions indicate that it is a diazo-compound. An acid barium salt was obtained, corresponding to the formula $Ba(O_2N_2)N_2O_2H_2$, the existence of which shows that hyponitrous acid is bibasic and has the formula $N_2O_2H_2$.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 1007 and 1258.)

On the Oxidation of Symmetrical Nitroxylene.

The researches of Remsen and his co-workers have shown that when an aromatic hydrocarbon which contains two hydrocarbon residues and a negative substituting atom or group is subjected to the action of chromic acid, that residue which is in the para or meta position is oxidized, whereas the residue in the ortho position is protected. E. WROBLEWSKY has now shown that when symmetrical nitroxylene, that is, the one in which each group is in the meta position with reference to both the others, is oxidized, both methyl groups are converted into carboxyl.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 1021.)

The Dismemberment of Tropine.

A. LADENBURG in a third communication on this subject shows that tropilene is converted by nitric acid into an acid of the formula of adipic acid, $C_6H_{10}O_4$, and probably identical with this. He has further found that, when tropidine is treated with bromine in sealed tubes, it is converted into dibrom-methylpyridine, ethylene bromide being formed at the same time. The reaction may be represented thus:

$$C_8H_{13}N + 4Br_2 = C_2H_4Br_2 + C_6H_5Br_2N + 4HBr.$$

This makes it appear probable that tropidine is a hydrogen addition product, and ethylene derivative of methylpyridine of the formula $C_5H_6(C_2H_4)NCH_3$. For tropine he suggests the formula $C_5H_7(C_2H_4(OH))NCH_3$.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 1028.)

Conversion of Pyrrol into Pyridine.

G. L. CIAMICIAN and M. DENNSTEDT have succeeded in obtaining monobrompyridine from pyrrol by the following method: Pyrrol potassium, C_4H_4NK, was treated with bromoform, when action took place, thus:

$$2C_4H_4NK + CHBr_3 = C_4H_4NH + C_5H_4BrN + 2HBr.$$

A careful comparison of the product with that obtained by the action of bromine on pyridine proved the identity of the two.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 1172.)

Action of Hydrogen Peroxide on Organic Matters and Fermentations.—On the Employment of Hydrogen Peroxide in Surgery.

MM. PAUL BERT and P. REGNARD have studied the action of hydrogen peroxide upon various forms of organic matter and upon fermentations, and find that it possesses very remarkable antiseptic properties. All fermentation due to an organized ferment is immediately and definitely arrested by hydrogen peroxide, the ferment is killed, and even after the removal of the hydrogen peroxide by one of the substances which destroys it most rapidly, the fermentation does not recommence. The yeast of beer is in this manner killed instantly, although it possesses itself the property of decomposing hydrogen peroxide. Specimens of wine, urine, and milk, each containing a few drops of hydrogen peroxide, have been exposed for several months in open vessels without exhibiting the least sign of alteration, while other specimens of the same identical liquids, without the addition of hydrogen peroxide, placed beside them, were in a state of complete decomposition. Although organized ferments are destroyed by hydrogen peroxide, soluble ferments do not seem to be affected by it, saliva, diastase, the gastric and pancreatic fluids continue to act in solutions containing hydrogen peroxide. MM. Bert and Regnard have also studied the action of hydrogen peroxide upon various organic materials, including the albuminoid substances, and all the tissues composing the animal body in a healthy or pathological state. The results of their investigations may be summed up as follows:

1. Hydrogen peroxide, even when very dilute, arrests fermentations due to the development of living organisms, and the putrefaction of all substances which do not decompose it.

2. It has no effect upon diastase fermentations.

3. Dilute hydrogen peroxide is not destroyed by fats, starches, soluble ferments, egg albumen, casein, the peptones, creatine, creatinine or urea.

4. It is rapidly destroyed by nitrogenous collagens, by musculin, fibrin of the blood, and various nitrogenous vegetable matters.

5. This action is definitely arrested by a temperature above 70°. Putrefaction, however, leaves it entirely intact.

As it appeared from the powerful antiseptic properties of hydrogen peroxide that it might prove of value in surgery, experiments were made upon the point by MM. PÉAN and BALDY at the hospital of St. Louis, with very successful results.

The hydrogen peroxide, in solutions containing from two to six times its volume of oxygen, according to the circumstances of the case, was used, both externally, as a dressing for wounds, ulcers, etc., and also given internally in certain affections, in doses of from three to five grains, containing six times its volume of oxygen. As a result of their experiments MM. Péan and Baldy consider themselves justified in stating:

1. Hydrogen peroxide containing, according to circumstances, from two to six times its volume of oxygen, appears to be capable of advantageously replacing alcohol and carbolic acid.

2. It can be employed, externally, for the dressing of wounds and ulcerations of all natures, in injections and in vaporizations, and internally,

3. The results obtained, even in the case of the largest operations, are, up to the present, in the highest degree satisfactory. Not only fresh wounds, but also old ones, proceed rapidly to cicatrization, and reunion by first intention of amputation wounds appears to be encouraged by this mode of dressing.

4. The general as well as the local state appears to be favorably influenced.

5. The advantages of hydrogen peroxide over carbolized water are its not having any poisonous effect nor unpleasant odor, while its application is entirely painless.

M. Bert calls attention to the fact that hydrogen peroxide for surgical use must be entirely neutral, while that obtained from the greater number of dealers in chemicals frequently contains a considerable quantity of sulphuric acid, so that its use would not be without danger.—(*Comptes rendus*, **94**, 1383, *and* 95, 49.)

R. D. C.

Disinfectants.

In an article[1] on disinfection Dr. R. Koch remarks that the only substances worthy of the name of disinfectants are chlorine, bromine, iodine, mercuric chloride, and perhaps potassium permanganate and osmic acid. He finds that spores of the bacillus of splenic fever, kept for many days in 5 per cent. zinc chloride solution, develop when placed in suitable nutritive liquids, even when added to serum containing ½ per cent. zinc chloride. He wonders how this salt could ever have been regarded as an antiseptic.

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[1] Mittheilungen des kaiserlichen Gesundheitsamtes **1**, 1881.

FR. BOILLAT, in criticising Koch's article, calls attention to the fact that for a substance to be an antiseptic it is not necessary for it actually to *destroy* germs. In the antiseptic treatment of wounds it would be impossible to employ such violently acting substances as those mentioned by Koch. All that is necessary is the presence of substances capable in some way of restraining the development of germs, which hence may properly be called antiseptics. Many antiseptics have the power of coagulating proteids. Boillat prepared such coagula from serum and egg albumin by precipitating with phenol, zinc chloride, copper sulphate and mercuric chloride. These albuminates, after being well washed to remove any excess of the precipitant, were mixed with a little water and exposed to the air. Pure serum and Koch's gelatine served to control the experiments. In the serum, gelatine and phenol-albuminate, bacteria appeared in 1, 1 and 2 days respectively, and marked putrefaction in 2, 4 and 6 days respectively, while in the metal-albuminates bacteria did not appear until from 31 to 45 days, and marked putrefaction in from 46 to 60 days. The surprisingly rapid putrefaction of the phenol-albuminate was explained when it was found on examination to contain no phenol. Splenic fever spores were found to develop in gelatine in 1 day, and not at all in metal-albuminates. According to Boillat, Koch did not add enough zinc chloride to his serum to convert all the proteids into the harmless but innutritious zinc-albuminate, and the spores availed themselves of the excess. Applied to the surface of a wound, zinc chloride forms a superficial coating of the neutral zinc-albuminate, which affords no means for the bacteria to develop, and protects the parts under it.

Experiments with iodoform (2 per cent. sol.); carbon tetrachloride, CCl_4; the chlorides C_2Cl_4 and C_2Cl_6, and bromo-toluene (liquid and solid), and dimethyl-pyrogallol (1 per cent. sol. each), as restraining putrefaction of pancreas, gave negative results, and paracresol was active only in solutions of at least ½ per cent., and even then did not restrain the action of the pancreatic ferment. —(*Journal für praktische Chemie*, [2], **25**, 300.) H. N. S.

On the Stannous Nitrates.

At the Royal Powder Works at Spandau, Prussia, frequent ignition of the powder at a certain stage of the process led to an examination of the machinery, when it was found that where at certain parts bronze pieces which were soldered were in constant contact with the moist powder, the solder was much corroded and in part entirely destroyed, and that in the joints had collected a substance which on being scraped out with a chisel, exploded with emission of sparks. It was suspected that the formation of this explosive material was in some way connected with the corrosion of the solder, and the subject was referred for investigation to RUDOLPH WEBER, of the School of Technology at Berlin. The main results of his investigation are here given.

The explosive properties of the substance indicated a probable nitro-compound of one of the solder metals (tin and lead), and as the lead salts are more stable and better understood than those of tin, it was resolved to investigate the latter, in hope of obtaining a similar explosive compound. Experiments on the action of moist potassium nitrate on pure tin led to no result, as no explosive body was formed. Stannous nitrate, $Sn(NO_3)_2$, formed by the action of dilute nitric acid on tin, has long been known, but only in solution, as it is decomposed on evaporating. By adding freshly precipitated moist brown stannous oxide to cool nitric acid of sp. gr. 1.20, as long as solution occurred, and then cooling the solution to —20°, Weber obtained an abundance of crystals of the composition $Sn(NO_3)_2 + 20H_2O$. They resemble crystals of potassium chlorate. They cannot be kept, as they liquefy at ordinary temperatures. An insoluble *basic* salt was obtained by digesting an excess of moist stannous oxide in solution of stannous nitrate, or by adding to a solution of stannous nitrate by degrees, with constant stirring, a quantity of sodium carbonate solution insufficient for complete precipitation. Thus obtained, the basic salt, which has the composition $Sn_2N_2O_7$, is a snow-white crystalline powder, which is partially decomposed by water, and slowly oxidized by long exposure to the air or by heating to 100°. By rapid heating to a higher temperature, as well as by percussion and friction, it explodes violently, giving off a shower of sparks. This compound is also formed when a fine spray of nitric acid (sp. gr. 1.20) is thrown upon a surface of tin or solder. It is also formed when tin or solder is exposed to the action of a solution of copper nitrate, and thus formed presents the properties already described.

In this, then, we have a probable cause of the explosions occurring in the powder works; but the explanation of the formation of the substance is wanting, as potassium nitrate was shown not to give an explosive substance with tin. A thin layer of a mixture of sulphur and potassium nitrate was placed between sheets of tin and copper foil, and allowed to stand, being kept constantly moist. After a time the copper was found to have become coated with sulphide, while the tin was largely converted into the explosive basic nitrate. The conditions are obviously the same as those found in the powder machinery, where bronze and tin solder are constantly in contact with moist gunpowder. The chemical action is probably this: the sulphur of the powder forms with the copper of the bronze, copper sulphide; this is oxidized to sulphate, which reacts with the nitre of the powder, forming potassium sulphate and copper nitrate; the latter, as shown above, then forms with the tin of the solder the explosive basic nitrate, which, being insoluble, gradually collects in the joints and finally leads to an explosion.—(*Journal für praktische Chemie*, [2], **26**, 121.)

H. N. S.

The Earth-Metals in Samarskite.

H. E. Roscoe has studied the group of rare earth-metals found in samarskite with a view to the separation of philippium. The coarsely powdered mineral was treated with hydrofluoric acid, which gave a greenish precipitate. This, after drying, was dissolved in sulphuric acid, and, after removing uranium by nitric acid, the earth-metals were precipitated by ammonium oxalate. The oxalates were converted by ignition into oxides, and these into nitrates, which were fused, dissolved in water, and from this solution the metals were separated into two groups by fractional precipitations from a solution of potassium sulphate. The more soluble of these two groups, containing the yttrium, philippium and terbium, after conversion of the sulphates into oxides, was treated with formic acid, and submitted to a long series of fractional precipitations. It was found impossible to obtain in this way the formate of a metal having a constant weight between 121 and 123, but the formate agreeing most closely with these numbers possessed distinct physical properties, differing very decidedly from those obtained from higher or lower fractions. In order to determine if this salt was a double formate of other metals, a mixture of two solutions of the formates of yttrium and terbium was made, and from this rhombic crystals were obtained with properties exactly like those attributed to philippium.—(*Journal of* (*London*) *Chemical Society* **41** (1882), 277.) J. R. D.

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VOL. IV. [JANUARY, 1883.] NO. 5.

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AMERICAN CHEMICAL JOURNAL.

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XIII.—ON THE ALKALINITY AND DIASTATIC ACTION OF HUMAN SALIVA.

BY R. H. CHITTENDEN AND J. S. ELY.

It is well known that human mixed saliva ordinarily possesses an alkaline reaction; as to the degree of alkalinity, however, but little has hitherto been definitely known. The same is true of the saliva from animals; but recently Herter,[1] in an analysis of the submaxillary secretion from a dog, found .090 per cent. of sodium carbonate, and this in saliva obtained by irritating the mucous membrane of the mouth with acetic acid.

Recent experiments[2] have plainly demonstrated that the addition of small quantities of sodium carbonate to saliva greatly impairs its diastatic action. It has therefore seemed to us desirable to ascertain the amount of alkali present in normal mixed saliva, also whether the alkalinity is subject to variation in different persons and at different times, and if so, whether there is any connection between variations of alkalinity and the diastatic action of saliva.

The saliva examined was obtained from fourteen different persons, all of whom, with one exception, were men between the ages of twenty and thirty. The secretion of the saliva was accelerated by chewing a small piece of pure rubber. The saliva was collected generally an hour or two after breakfast, in quantities of 50 cc., and was at once filtered through paper in an atmosphere free from ammonia. A portion of the filtered fluid was then at once neutralized with a standard acid solution to determine the alkalinity, while another portion was used in the determination of the diastatic action. Great care was taken to have all the dishes used perfectly clean and dry, so that there might be no dilution or contamination of the saliva.

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[1] Published in Hoppe-Seyler's Physiologische Chemie, p. 192.

[2] This Journal, **3**, 305; also **4**, 121.

The method adopted in the determination of the alkalinity was as follows: 25 cc. of the filtered saliva were mixed with twenty drops of an alcoholic solution of cochineal and about 10 cc. of pure water, and then titrated directly with a dilute solution of hydrochloric acid in a room carefully guarded from ammoniacal fumes. The main difficulty attending the titration was the turbidity or precipitation produced in the saliva when the neutral point was nearly reached, thereby obscuring the change of color in the indicator. Cochineal was found to work to the best advantage; but as the precipitate produced by neutralization was insoluble in excess of acid, it made it difficult to use the perhaps better method of adding an excess of acid and then titrating back with standard alkali. The standard acid was made of such strength as to contain approximately .2 per cent. HCl. Titration with standard solution of silver nitrate showed that it actually contained .19 per cent. HCl, consequently 1 cc. of the standard acid was equivalent to .00276 gram Na_2CO_3.

A few determinations of the alkalinity of several specimens of saliva were then made to ascertain the amount of dilute acid required in a single determination, after which a standard solution of pure sodium carbonate was made of such strength that 1 cc. contained .0018292 gram Na_2CO_3. With this solution the dilute acid was standardized, under exactly the same conditions as the saliva was subjected to, with the following results:

12cc	Na_2CO_3 sol.	required	7.87cc	HCl sol.,	1cc	HCl sol.	=.00278	gr Na_2CO_3
12	"	"	7.87	"	1	"	=.00278	"
8	"	"	5.17	"	1	"	=.00281	"
12	"	"	7.67	"	1	"	=.00286	"
12	"	"	7.78	"	1	"	=.00280	"
24	"	"	15.69	"	1	"	=.00279	"
24	"	"	15.69	"	1	"	=.00279	"

Average, 1cc. standard HCl sol.=.00280 gram Na_2CO_3.
Calculated 1cc. " " =.00276 " " "

It is thus apparent that the error attending the use of such a dilute acid solution under these circumstances is inappreciable, and the results obtained in the analyses of the different samples of saliva may be looked upon as accurately expressing the degree of alkalinity.

The diastatic action of the saliva was determined in each case as follows: .5 gram of starch was heated to boiling with 40 cc. of water in a small flask, and when cold 12 cc. of the filtered saliva were added from an accurately calibrated burette, and the mixture placed at 40° C for 30 minutes. At the end of this time all further diastatic action was stopped by boiling the fluid. When cold, the mixture was diluted with water to 200 cc., and in 50 cc. or one-fourth of the filtered fluid, sugar was determined gravimetrically by the use of the method so carefully elaborated by Maercker[1] and others. From the weight of metallic copper, the amount of reducing substance calculated as dextrose was ascertained by the use of the reduction equivalents experimentally determined by Maercker.[2]

The following tables show the results obtained:

Collector.	Time.	Alkalinity.			Diastatic Action.	
		HCl sol. required.	Equivalent in Na_2CO_3.		Wt. Cu. in one-fourth.	Percentage of sugar formed.
A	March 1	5.62 cc.	.015736 gram.	.063 per ct.	.1052 gram.	42.77 per ct.
“	“ 2	5.25 “	.014700 “	.059 “	.1130 “	45.94 “
“	“ 3	5.71 “	.015988 “	.064 “	.1089 “	44.28 “
“	“ 8	5.40 “	.015120 “	.061 “	.1116 “	45.37 “
“	“ 9	5.66 “	.015848 “	.063 “	.1141 “	46.39 “
“	“ 10	5.24 “	.014672 “	.058 “	.1137 “	46.23 “
“ [3]	“ 10	8.43 “	.023604 “	.094 “	.1061 “	43.14 “
“	“ 16	5.11 “	.014308 “	.057 “	.1160 “	47.26 “
“	“ 17	5.29 “	.014812 “	.059 “	.1152 “	46.93 “
“	“ 24	5.30 “	.014840 “	.059 “	.1110 “	45.13 “
“	“ 28	5.94 “	.016632 “	.066 “	.1070 “	43.51 “
“ [3]	April 2	8.14 “	.022792 “	.091 “	.1070 “	43.51 “
	Average.			.061 per ct.[4]		45.03 per ct.

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[1] Die Landwirthschaftliche Versuchs-Stationen, **25**, 115-116; also this Journal, **3**, 308.

[2] *Loc. cit.*

[3] Stood 12 hours before being examined.

[4] Exclusive of the two which stood 12 hours.

Collector.	Time.	Alkalinity.			Diastatic Action.	
		HCl sol. required.	Equivalent in Na_2CO_3.		Wt. Cu. in one-fourth.	Percentage of sugar formed.
B	March 2	13.29 cc.	.037212 gram.	.149 per ct.	.1022 gram.	41.58 per ct.
"	" 3	11.06 "	.030968 "	.124 "	.1000 "	40.66 "
"	" 9	13.77 "	.038556 "	.154 "	.0974 "	39.63 "
"	" 24	14.59 "	.040852 "	.163 "	.1194 "	48.64 "
"	" 31	11.78 "	.032984 "	.132 "	Lost.	
"[1]	April 2	11.64 "	.032592 "	.130 "	.1018 "	41.42 "
	Average.			.144 per ct.[2]		42.38 per ct.
C	March 2	5.01 cc.	.014028 gram.	.056 per ct.	.1062 gram.	43.18 per ct.
"	" 3	4.67 "	.031076 "	.052 "	.1020 "	41.50 "
"	" 10	5.16 "	.014448 "	.058 "	.1050 "	42.69 "
"[1]	" 10	5.00 "	.014000 "	.056 "	Lost.	
"	" 17	4.57 "	.012796 "	.051 "	Lost.	
"	" 28	8.50 "	.023800 "	.095 "	.1026 "	41.74 "
	Average.			.062 per ct.[2]		42.27 per ct.
D	March 2	5.81 cc.	.016268 gram.	.065 per ct.	.1083 gram.	44.04 per ct.
"	" 9	7.47 "	.020916 "	.084 "	.1069 "	43.46 "
"	" 16	6.95 "	.019460 "	.078 "	.1095 "	44.52 "
"	" 17	7.26 "	.020328 "	.081 "	.1058 "	42.94 "
"	" 24	8.41 "	.023548 "	.094 "	.1010 "	41.09 "
"	" 28	4.81 "	.013468 "	.054 "	.1029 "	41.86 "
	Average.			.076 per ct.		42.98 per ct.
E	March 2	6.79 cc.	.019012 gram.	.076 per ct.	.1062 gram.	43.18 per ct.
"	" 17	8.18 "	.022904 "	.092 "	.1071 "	43.55 "
"	" 24	7.52 "	.021056 "	.084 "	.1268[3] "	51.91 "
"	" 28	7.33 "	.020524 "	.082 "	.1029 "	41.86 "
	Average.			.083 per ct.		45.12 per ct.
F	March 10	7.17 cc.	.020076 gram.	.080 per ct.	.1014 gram.	41.25 per ct.
"	" 10	7.47 "	.020916 "	.084 "	.0991 "	40.32 "
"	" 16	7.34 "	.020552 "	.082 "	.0995 "	40.52 "
"	" 17	7.70 "	.021560 "	.086 "	.0961 "	39.10 "
"	" 28	6.64 "	.018592 "	.074 "	.0961 "	39.10 "
"	" 31	7.79 "	.021812 "	.087 "	.0946 "	38.48 "
	Average.			.082 per ct.		39.79 per ct.
G	March 16	9.83 cc.	.027524 gram.	.110 per ct.	.1056 gram.	42.93 per ct.
"	" 17	8.72 "	.024416 "	.097 "	.1028 "	41.82 "
"	" 28	9.86 "	.027608 "	.110 "	.1029 "	41.86 "
"	" 31	9.29 "	.026012 "	.104 "	.1015 "	41.29 "
	Average.			.105 per ct.		41.97 per ct.

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[1] Stood 12 hours before being examined.

[2] Exclusive of the one which stood 12 hours.

[3] This result is probably too high, although no error in the analysis could be detected.

Collector.	Time.	Alkalinity.			Diastatic Action.	
		HCl sol. required.	Equivalent in Na_2CO_3.		Wt. Cu. in one-fourth.	Percentage of sugar formed.
H	March 24	5.24 cc.	.014672 gram.	.059 per ct.	.1054 gram.	42.85 per ct.
“	“ 31	6.01 “	.016828 “	.067 “	.1022 “	41.58 “
	Average.			.063 per ct.		42.21 per ct.
I	March 28	7.24 cc.	.020272 gram.	.081 per ct.	.1031 gram.	41.95 per ct.
“	“ 31	3.30 “	.009240 “	.037 “	.1016 “	41.33 “
	Average.			.059 per ct.		41.64 per ct.
J	March 28	8.77 cc.	.024556 gram.	.098 per ct.	.1011 gram.	41.13 per ct.
“	“ 31	7.88 “	.022064 “	.088 “	.0950 “	38.65 “
	Average.			.093 per ct.		39.89 per ct.
K	March 31	5.87 cc.	.016436 gram.	.066 per ct.	.1109 gram.	45.09 per ct.
“	April 3	5.53 “	.015484 “	.062 “	.1107 “	45.01 “
	Average.			.064 per ct.		45.05 per ct.
L	March 31	7.06 cc.	.019768 gram.	.079 per ct.	.1017 gram.	41.37 per ct.
“	April 3	8.07 “	.022596 “	.090 “	.1151 “	46.89 “
	Average.			.084 per ct.		44.13 per ct.
M	April 3	6.86 cc.	.019208 gram.	.077 per ct.	.1125 gram.	45.74 per ct.
N[1]	“ 2	7.06 “	.019768 “	.079 “	.1016 “	41.33 “

The average alkalinity for these 51 samples of saliva expressed in the form of sodium carbonate is .080 per cent. The average diastatic action of 54 samples of saliva expressed in the percentage of sugar formed from the starch is 42.82 per cent. A glance at the individual results obtained shows several interesting facts, which may be briefly summarized as follows:

1. Saliva from different individuals may show a constant difference in alkalinity as in A, B, F and G, although in the majority of cases the alkalinity varies only within narrow limits.

2. Saliva secreted by the same individual at different times has within certain limits a constant degree of alkalinity.

3. While saliva from different individuals shows in several cases a decided and constant difference in alkalinity, there is no corresponding difference in diastatic action which is at all constant. We are thus forced to the conclusion that the variations of alkalinity are within too narrow limits to exercise any appreciable influence on the diastatic action of the saliva.

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[1] Stood 12 hours before being examined.

DETERMINATION OF ORGANIC MATTER IN POTABLE WATER.

By Prof. J. W. Mallet, F. R. S.

(*Concluded from page* 263.)

SANITARY CONCLUSIONS AND INTERPRETATION OF RESULTS.

To admit of easier comparison, the results by the chief processes examined have been thrown into graphical form in Tables XIX and XX, of which the former refers to the natural waters and the latter to those artificially prepared.

(These tables will appear with the general report.)

Chemical results contrasted with actual sanitary history of the natural waters examined.

1. An inspection of Table XIX shows that *no strongly marked generic difference is presented by the results from any of the processes for the estimation of organic matter or its elements between the generally wholesome waters of Class* I *and the medically condemned and fairly assumed as pernicious waters of Class* II. Judging by the general impression of the curves upon the eye, one would be inclined to attribute somewhat more importance to the results involving nitrogen than to those dependent upon carbon; but neither will afford the means of broadly distinguishing the two classes. This conclusion is otherwise illustrated by the figures in Table XXI.[1]

It will be seen from this table that no marked difference exists between the *highest*, *lowest* or *average* result obtained by any of the processes for the waters of Class I and the corresponding result for those of Class II. No one could, with these figures to guide him, refer a water of unknown origin to one or the other of the two classes on the evidence afforded by chemical analysis, using any or all of the processes in question. The most varied results presented in Class III admit of being studied with some interest in connection with the history of the individual waters, but are not available for the main purpose of testing the chemical methods, as this class includes only waters the sanitary character of which in advance of examination was more or less doubtful—waters under suspicion only.

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[1] See next page.

TABLE XXI. — *Comparison of chemical results for waters of Classes* I *and* II.

	Least result.		Greatest result.		Average.	
	Class I.	Class II.	Class I.	Class II.	Class I.	Class II.
Organic carbon	.36	.33	7.20	7.79	2.36	2.08
Organic nitrogen.........	.08	.03	1.41	6.88[1]	.56	.94[2]
Sum of organic carbon and nitrogen.	.44	.61	7.86	8.31[2]	2.92	2.92[2]
Nitrogen of free ammonia.	.008	.008	.675	.295	.092	.090
Nitrogen of albuminoid ammonia.	.016	.021	.268+	.214	.112	.099
Nitrogen of total ammonia.................	.028	.033	.704	.343	.204	.189
Oxygen consumed in one hour (Tidy).......	.062	.082	4.008	3.340	.995	.791
Oxygen consumed in three hours (Tidy) ...	.210	.104	5.212	4.188	1.305	1.065
Oxygen consumed (Kubel).	None.	None.	7.443	6.000	2.140	1.271

2. Making the most liberal allowance for the imperfection of the different processes for the estimation of organic matter or its constituents, it is well worthy of notice how very small is the absolute amount of organic matter indicated as present in many of the most dangerous waters, an amount so small as to furnish important evidence against any chemical theory of the production of disease from this source, any theory based on the simple assumption that some of the chemical products of the decomposition of organic matter are poisonous or noxious in their effect upon the human system. Thus, if *the whole* of the organic carbon and nitrogen found in such waters as Nos. 35 and 36, of the highly dangerous character of which there can scarcely be a doubt, existed as strychnine, it would be necessary to drink about half a gallon of the water at once in order to swallow an average *medicinal* dose of the alkaloid. It is not easy to believe that the ptomaines, or any other chemical products of putrefactive change as yet observed, can possess an intensity of toxic power so very much greater than that of the most energetic of recognized poisons. While numerous facts

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[1] This figure is undoubtedly too high, in consequence of incomplete reduction of nitrates. The next highest is 2.36, and even this is probably higher than the truth, for the same reason.

[2] Including the no doubt erroneous highest single figure.

go to support the belief that, not to the effect of any chemical substances (such effect necessarily standing in definite relation to their quantity), but to the presence of living organisms with their power of practically unlimited self-multiplication, we must in all probability look for an explanation of, most at any rate, of the mischief attributable to drinking water, it is of course possible that indirectly a large amount of organic matter in water may be more dangerous than a smaller quantity, as furnishing on a greater scale the suitable material and conditions for the development of noxious as well as harmless organisms.[1]

Whether variations in the mere quantity of organic matter, within such limits as occur in water at all likely to be used for drinking, are of much importance in this respect, *i. e.* as determinant of the presence or abundance of organisms, is a question which may be asked, and on it depends, I think, largely the utility of all attempts to determine or estimate the quantity of organic matter or its constituents as such.

3. A much more conspicuous difference between the waters of Classes I and II is presented by the results for nitrites and nitrates as shown in Table XXII.

In this table a tenfold height is given to the ordinates representing the nitrites, the smaller quantity in which they occur requiring this exaggeration.

Here we find a very obvious connection between the results of chemical examination and the known sanitary character of the several waters, the salts of nitrous and nitric acid being either absent or present in but trifling amount in the waters of Class I, believed to be wholesome; almost universally present, and in many cases in large quantity, in the pernicious waters of Class II, and very variable as to presence and amount in the waters grouped together under the doubtful head of Class III. No aspect in which I have compared together the good and bad natural waters has afforded so definite a result as this.

This result is worthy of special attention in view of the different opinions which have been expressed as to the sanitary significance of nitrites and nitrates in water. Thus, Wanklyn says:[2] "The nitrates and nitrites have been erroneously regarded as measuring

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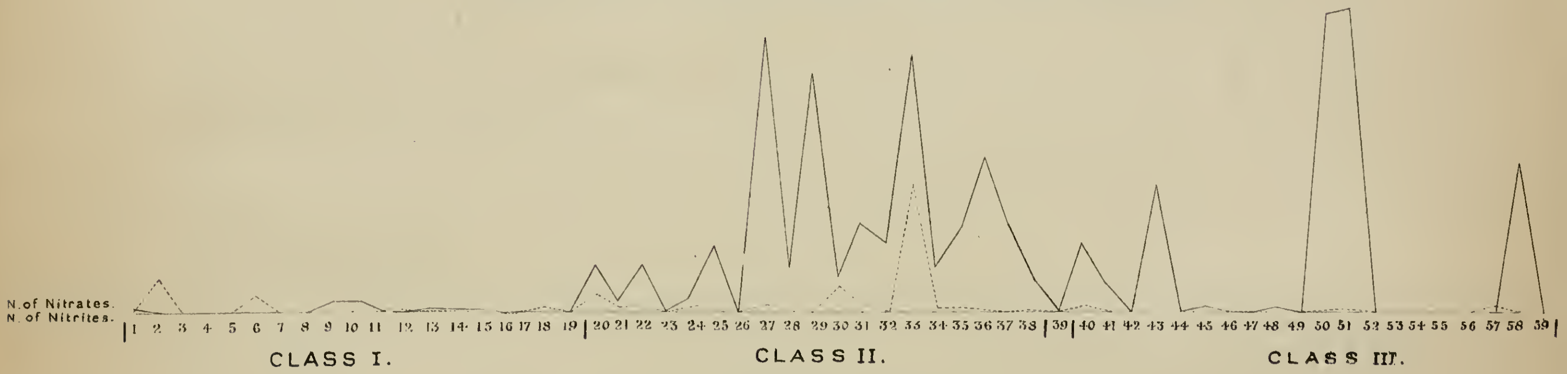
[1] Tiemann and Preusse have suggested that a polluted water may more *probably* contain disease ferments than a pure one, but it should not be inferred that an impure water is necessarily pernicious. Quoted in Chem. News, January 16, 1880, 30, 31.

[2] J. A. Wanklyn, "Water Analysis," Lond., 1879, 97, 98.

TABLE XXII.–Nitrites and Nitrates in natural waters examined.



I. FRIEDENWALD, LITH-BALT°.

the defilement of water." "In fine, presence or abundance of nitrates does not show defilement by means of sewage, and deficiency of nitrates does not show absence of defilement. Many excellent waters have been condemned as unwholesome on account of the nitrates contained by them; and it cannot too strongly be insisted upon that the nitrates afford no data of any value in judging of the organic quality of a water." Angus Smith says:[1]

"There are many interesting questions to be asked regarding nitrates. I am inclined to think that their presence shows that the most dangerous state of the organic matter is past. When they appear in any solution, the chief escape of putrid gas seems to have ceased; the water may, however, be still dangerous to use, and, of course, is revolting to the imagination." . . . [2]"Those nitrates, however, which do remain indicate that at least an equivalent of albuminous matter or sewage matter *did* exist."

Frankland clearly expresses his views[3] as to this evidence of "previous sewage contamination" thus:

"Large quantities [of nitrates] convict water of previous pollution by organic matters of animal origin. They tell only of the contamination which is past; but, by inference, they also declare the probable nature of the organic matter now present. . . . . . Whether or no the analyst should form an unfavorable opinion of the water from the amount of nitrates must depend upon the proportion of organic matter actually present, and on his confidence in the efficiency and uniform action of the purifying process."

As the basis of his determination of "previous sewage contamination" Frankland takes the sum of the nitrogen present as ammoniacal salts, nitrites, and nitrates, diminished by an allowance for the average amounts of these substances in rain-water; he therefore treats the significance of the ammonia as the same with that of the nitrites and nitrates, as evidence merely of the past presence of nitrogenous organic matter of which a part *may* remain.

Griess has expressed a strong opinion[4] as to the sanitary importance of detecting nitrates, and the unfitness of water for drinking purposes when containing them.

Ekin[5] attaches very great importance to the presence of nitrates and nitrites. Thus he says:

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[1] Chemical News, September 3, 1869, 113.

[2] Chemical News, June 25, 1869, 305.

[3] "Water Analysis for Sanitary Purposes," 27.

[4] Ann. d. Chem. u. Pharm. **154**, 336.

[5] "Potable Water," 2d ed., Lond. 1880, pp. 15, 16, 22, 25, 26, 27, 28, &c.

"Waters which have undoubtedly given rise to typhoid fever have been found by the writer over and over again not to contain more than 0.05 part of albuminoid ammonia in 1,000,000, and which, notwithstanding their containing a large excess of nitrates, have been passed by analysts of undoubted ability as being fit for drinking purposes. The attention of the writer was particularly drawn to this in the case of a district where typhoid fever was hardly ever absent, and where the conditions were such as pointed exclusively to water as being the aggravating cause. . . . Samples were taken when the pollution was evident and analyzed. Two only were found to contain an excess of albuminoid ammonia, but all contained a large excess of nitrates. . . . The significance of an excess of nitrates has already been sufficiently dwelt upon, and we have seen that both upon *a priori* grounds and as the result of actual experience, their presence in abnormal quantity is objectionable. . . . When the amount [of nitrates] exceeds 0.5 or 0.6 part [per 100,000], it points significantly to dangerous pollution; . . . nitrogen as nitrates should be invariably absent from a good water. . . . This view of the importance to be attached to an abnormal quantity of nitrates has been formed in spite of a considerable predisposition to a contrary opinion, and has been literally forced upon the writer again and again by the investigation of cases which really leave no doubt in the matter."

Reuben Haines, of Philadelphia, has furnished [1] the details of some cases in his own experience, which he says are "in partial corroboration of the opinions of Mr. Ekin."

Among the artificially polluted waters of the investigation now reported on, there are a number of samples of such general character as to attach to them the gravest suspicion on sanitary grounds, suspicion corroborated in sundry cases by the biological tests applied to them; in which, nevertheless, nitrates and nitrites are not found; but in these waters we find the quantity of organic matter extraordinarily large, and generally accompanied by very large amounts of ammonia—*e. g.* Nos. 119, 120, 121, containing water in which the dead body of an animal had been allowed to macerate; Nos. 122, 123, 124 containing much blood from a slaughter-house, and Nos. 137 and 138 containing the dejecta from typhoid-fever patients.

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[1] "Methods for judging of the wholesomeness of drinking-water." From Journal of the Franklin Institute, February, 1881.

Looking at the results from the natural waters of Classes I and II, and bearing in mind the conclusions reached by Müller, Schloesing and Müntz, Storer, Warington, and others[1] as to the process of nitrification being due to the presence of an organized ferment or ferments of bacterial character, the idea suggests itself whether the noxious character of waters containing largely of nitrates and nitrites—themselves presumed to be harmless—and but very little organic matter—which ought to be present, of some sort, to support the "previous contamination" view—*may not be in reality due to the presence of a special nitrifying ferment, itself to be classed among the lower organisms capable of propagating disease.*

4. Two points require to be borne in mind, suggestive of caution in drawing such conclusions as the above in regard to the sanitary in connection with the chemical character of water.

In the first place the samples examined may possibly have undergone chemical change in the interval from their collection to their reaching the analysts, so that, for example, organic matter may have disappeared or nitrates may have been formed. With the precautions taken to lose as little time as possible, there does not seem much likelihood of such changes having occurred to so serious an extent as to essentially alter the character of the water.

In the second place, with the object which I had in view, of obtaining samples of water capable of producing disease, it was necessary to take what may be called *exaggerated instances* of mischief—well-marked or comparatively violent cases of illness—since no others could well be traced with sufficient strength of probability to their supposed cause, and it may very possibly be that the organic impurities present in the waters concerned in such cases are not the same as those which would produce slighter, but in time serious, ill effects. Slighter forms of disease, in reality attributable to drinking-water, may perhaps be numerous, and possibly of various types; but generally the difficulty will be too great of securing, in view of the many factors concerned, any satisfactory evidence as to their cause. The collection of strongly marked cases only, neglecting slighter ones if such exist, involves to some extent the same fault in principle as the commonly applied test of the death-rate for particular diseases in the discussion of local sanitary conditions; there may be numerous cases of illness, with but few deaths. The same difficulty also is experienced in trying pathological experiments on the lower animals; only strongly marked effects can be noted or satisfactorily connected with their supposed cause.

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[1] Comptes rendus, **84**, 301; **85**, 22, 1018. Jour. Chem. Soc. (Lond.), January, 1878, 44; July, 1879, 429. Chem. News, November 4, 1881, 217, &c.

5. In regard to the comparatively rough determinations of chlorine, the results are, in many of the cases of water from shallow wells, significant enough of contamination by fluid animal excreta. The amounts of chlorine found in specimens Nos. 2, 3 and 4 of water from the deep artesian well at Charleston, S. C., and in No. 22 from a well near the sea on Staten Island, and Nos. 50 and 51 from a well, and No. 52 from a pond in the neighborhood of the sea at Newport, R. I., illustrate the need for thought as to the natural source of a water in drawing conclusions in connection with the presence of chlorides. Even in cases in which chlorine has come in with organic matter, the impropriety of too hastily deciding, as is sometimes done, that a small quantity indicates vegetable and a large amount animal contamination, is illustrated by the results for No. 65, containing an infusion of hay or dry herbage,[1] and for Nos. 87 and 88, containing the alkaline washings from wood pulp at a paper-mill, in contrast with those for Nos. 120 and 121, containing a very foul infusion of the body of a dead animal, and for Nos. 138 and 139, containing morbid animal matter from cases of typhoid and scarlet fever.

Biological results contrasted with the actual character of the waters examined.

The lists of waters marked (independently) by Professor Martin and Dr. Hartwell as "dangerous" and "suspicious," on the basis of the biological observations, are summarized, in connection with the classes represented, in Table XXIII.

TABLE XXIII.—*Biological classification of waters.*

Class.	No. in class.	Professor Martin.		Dr. Hartwell.	
		Dangerous.	Suspicious.	Dangerous.	Suspicious.
I	19	...	4	...	7
II	19	...	2	...	1
III	20	2	1	1	3
IV	20	3	3	3	2
V	21	4	5	2	10
VI	21	4	1	1	6
VII	15	4	3	4	7
VIII	4	1	2	2	1

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[1] It is possible that salt may have been sprinkled over this hay in curing it, as is sometimes done, though I have no special reason to suppose so. It was upland, not salt-marsh hay.

1. It is evident on inspection of this table for Classes I to III, that, as has been remarked on a previous page, the biological methods employed will not afford the means of deciding between a wholesome and an unwholesome natural water. Several of the waters believed to be fairly wholesome for human consumption, certainly in use for drinking purposes on a large scale, are marked "suspicious," while not one of the waters believed to have proved themselves pernicious when used by man are set down as "dangerous."

2. In many cases the waters which produced most decided effects upon the rabbits contained *very large* amounts of organic matter, so large as to probably invalidate a comparison with the natural waters or with much more dilute specimens of artificial preparation.

3. On the other hand, we find in several instances, on comparing the pathological results from three different strengths of a solution of the same organic material, that it is not the strongest which has produced the most marked effects.

4. In probable support of the idea that it is not mainly the quantity of organic matter, but the presence and nature of low organisms which render drinking water unwholesome, such cases deserve attention as No. 83 in contrast with Nos. 84 and 85, and also Nos. 131, 132 and 133 (if the deaths of comparison rabbits be not considered to vitiate the results) in contrast with Nos. 134, 135 and 136. Here the pernicious character of waters containing relatively but very little organic matter seems to be distinctly indicated.

5. It is pretty plain that much difficulty in the interpretation of the biological results arises from too great differences of absolute strength in the solutions of organic matter used. In any future attempt to extend investigation in this direction it would be well to more nearly equalize the dilution, though it might perhaps prove necessary to use in all cases more organic matter than is usually found in potable water of natural origin.

Chemical results as to animal in contrast with vegetable organic matter in water.

1. In general the conclusions are sustained which have been usually drawn in regard to the source of organic matter, based on the more highly nitrogenous character of that from animal than that from vegetable *debris*. This remark applies to the ratio of

organic C : N obtained by the combustion process (although the value of the figures is much reduced by the errors in the method which have been pointed out), and also to the amounts of albuminoid ammonia obtained, and the consumption of oxygen from acid permanganate.

2. But the necessity for caution in drawing such conclusions, or the propriety of substituting for the statement that a given water is polluted by, say, animal matter, rather the simple assertion that the polluting material is of highly nitrogenous character, is illustrated by such cases as Nos. 89, 90, and 91, containing the alkaline washings from the manufacture of starch, and Nos. 98, 99, and 100, containing the refuse from canning tomatoes. These waters might well be supposed to be contaminated with animal matter from the evidence afforded by the chemical results, interpreted in the usual way.

3. On the other hand, the results for Nos. 104, 105, and 106, containing a watery infusion of human fæces, especially the C : N ratio, might be taken to indicate the presence of vegetable matter. This fact, well deserving attention from a sanitary point of view, is opposed to the evidence of pollution obtained where urine alone is concerned, and might modify the conclusions drawn in cases involving drainage from mixed solid and fluid excreta. The fact itself is intelligible in view of the tendency to accumulation and ultimate rejection from the intestines of the vegetable fibre[1] of our food and the products of its limited alteration, as well as the highly carbonaceous character of the biliary discharges.

4. The different rate of removal from water of organic carbon and organic nitrogen is in one form illustrated by the comparison of No. 119 with No. 120 and No. 121, all three containing the watery liquid in which the body of a dead animal had been macerated, as also No. 128 in contrast with Nos. 129 and 130, all containing washings from wool. The true effect of the changes taking place in the water is, however, blended with and partially obscured by the effect of difference of strength on the errors which have been pointed out belonging to determinations by the combustion process. The bearing of such changes in the C : N ratio, from both causes, on the conclusions to be drawn as to the source of pollution is very obvious.

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[1] The infusion used was strained, but not filtered. It contained a good deal of very fine suspended material.

5. Dr. Smart, in interpreting his results by the albuminoid-ammonia process, aided, however, in some cases, by his application of the Kubel form of the permanganate process, has for most of the waters in which the organic matter was of known character (though unknown at the time to *him*) attempted to distinguish between that of vegetable and that of animal origin, and his conclusions are given in column 45 of Table X. On examining these it will be seen that in a very large proportion of cases he has been right, while some of those in which his deductions are incorrect are intelligible in the light of full consideration of all the facts. Thus, he has referred Nos. 105 and 106, containing infusion of human fæces, to the class of vegetable matter, this case having been alluded to above; and Nos. 108 and 109, containing drainings from a pile of stable manure, to the same class, this being in many respects an analogous case, and, indeed, a more strongly marked one of its kind.

Biological results as to animal in contrast with vegetable organic matter in water.

1. Decidedly the most noteworthy result under this head is the well-marked pathological effect produced upon rabbits by the injection of waters contaminated solely by such vegetable matter as would usually be esteemed harmless. An account has been given on previous pages of the general report of the repeated experiments with water containing an infusion of dead forest leaves (No. 68), all leading to essentially the same result. A like effect followed from the experiments with the peaty waters of the Dismal Swamp (Nos. 78 and 79).

While there have hitherto been occasional allusions by sanitary writers[1] to slight indisposition now and then experienced by persons drinking the peat water of mountain streams, it has been usually assumed that peaty water is *not* unwholesome, strong language on this head being often used,[2] and that, in general, organic matter of vegetable origin is harmless, or comparatively harmless, while that of animal origin is highly dangerous.[3] The results above referred to indicate that, under the special conditions of the experiments with rabbits, vegetable matter representing mainly or largely alteration products of woody fibre may be in a high degree pernicious.

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[1] Angus Smith, in Chem. News, June 25, 1869, 304. Ekin, "Potable Water," p. 15, footnote. 6th Report of Pollution of Rivers Commission, p. 34.

[2] Tidy, Jour. Chem. Soc. (Lond.), Jan. 1879, 65. Ekin, "Potable Water," p. 15.

[3] Frankland, "Water Analysis," 93-97. Tidy, Jour. Chem. Soc. (Lond.), Jan. 1879, 80–83. Ekin, "Potable Water," pp. 12, 13, 14, 15, &c. R. Haines, Methods for judging of wholesomeness of drinking waters, p. 11. De Chaumont, Arch. Ch. Pharm. XVII, 124.

2. It will be seen that for nearly all the waters classed as "dangerous" by Professor Martin and Dr. Hartwell the ratio of organic C : N was rather high.

3. The above conclusion as to the apparent possibility of vegetable organic matter proving itself decidedly injurious has to be qualified by observing that in the well-marked cases of such results the amount of organic matter present in the water was large, and it would not be safe to affirm on this evidence alone that similar waters, if diluted to the ordinary potable standard,[1] would still prove themselves capable of causing disease or death in the animals experimented on; indeed, the evidence tends rather the other way, so far as the experiments go which were made by injecting the rabbits with *the same quantities* of weaker solutions. But, on the other hand, water containing as much vegetable organic matter as No. 78 is often used for drinking purposes in peaty districts, and this very Dismal Swamp water has often been taken by choice as the supply for ships leaving port, and has been spoken of as a source of supply for the city of Norfolk; so that the discussion of wholesomeness or unwholesomeness of such water is not without practical interest.

4. If the theory be accepted, which has so much in its favor, attributing the production of disease by organic matter in drinking water not to any specifically poisonous *substance* or substances, but to the presence and action of living organisms, it seems quite conceivable that a water containing organic matter of any kind, including vegetable matter, may be harmless at one time, and harmful at another, when perhaps a different stage of fermentation or putrefactive change may have been entered upon, and special organisms may have made their appearance or entered upon a new phase of existence. Thus there might possibly be safety in drinking a peaty water, or water filtered through beds of dead forest leaves, when fresh, danger when after a certain amount of atmospheric exposure bacterial organisms had become developed, and safety again, perhaps, after the growth of such organisms had fallen off and more or less of the available organic matter had been consumed. I have been informed that old ship-captains who have often carried the water of the Dismal Swamp to sea entertain a

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[1] See 6th Report of Pollution of Rivers Commission, p. 34.

belief that this water undergoes a "kind of fermentation," after which it becomes remarkably good and wholesome. In support of some such idea as to different stages passed through by water (containing vegetable matter) as to the development of organisms and sanitary character, leading to the possibility, on its being stored, of wholesomeness at one time and unwholesomeness at another, the microscopical and biological reports of Nos. 62, and 69, 70, and 71, are worthy of notice.

Evidence afforded by chemical results as to putrescent or non-putrescent character of organic matter in water.

1. Tidy has claimed[1] as one of the merits of the permanganate process, that it enables the distinction to be drawn between "putrescent and easily oxidizable" and "non-putrescent or less easily oxidizable" organic matter, and has given the results of some experiments to show that the former are, for the most part at any rate, disposed of within the first hour; hence his rule as to determining separately the consumption of oxygen in that time and in three hours, and comparing the results, by means of which comparison he says "we obtain data of great value by which to judge the nature of the organic impurity." In column 28 of Table X, I have given the ratio of the consumption of oxygen from permanganate used as directed by Tidy in 1 hour to that in 3 hours, the latter quantity assumed = 100. The results for those waters, the nature of the organic matter in which was known, are obviously affected variously by sundry conditions, such as the different strengths of solutions, the presence together of both easily and less easily oxidizable matter, &c., but on the whole do not afford much support to the opinion expressed by Tidy. He distinctly assumes animal matter to be, at any rate as a rule, more "putrescent and easily oxidizable" than vegetable matter, but on examining the percentages in column 28, taking the averages for the different classes of waters, we find—

	Per cent.
Organic matter of vegetable origin:	
For Class IV	84.0
For Class V	80.8
Organic matter of animal origin:	
For Class VI	74.5
For Class VII	77.6
For Class VIII	79.0

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[1] Jour. Chem. Soc. (Lond.) Jan. 1879, 78, 81, 82.

Thus, although the differences are not very great, the proportionate consumption of oxygen within the first hour is rather greater for those waters containing vegetable than for those containing animal matter. Again, judging merely by appearance, smell, &c., I should say that the waters in the foulest and most actively putrescent condition were those containing the alkaline washings from a starch factory (Nos. 89, 90, 91), the washings from the bag-filters of a sugar refinery (Nos. 92, 93, 94), the refuse from canning tomatoes (Nos. 98, 99, 100), infusion of human fæcal matter (Nos. 104, 105, 106), infusion of the body of a dead animal (Nos. 119, 120, 121), mixed drainings from a slaughter-house (Nos. 125, 126, 127), and the dejecta from typhoid-fever patients (Nos. 137, 138); the average consumption of oxygen for all of these in one hour is 80 per cent. of that in three hours; almost exactly the same with the mean of all the above figures for the five classes examined (giving them equal value), viz. 79.2 per cent.

2. On the other hand, Dr. Smart has expressed the opinion, based upon his previous extensive experience with the albuminoid-ammonia process, aside from his work with it in connection with the present investigation, that *gradual* evolution of albuminoid ammonia indicates the presence of organic matter, whether of vegetable or animal origin, in a fresh, or comparatively fresh, condition, while *rapid* evolution indicates that the organic matter is in a putrescent or decomposing condition. In column 45 of Table X will be found his application of this principle of interpretation to his results obtained from the waters examined; the detailed facts as to the rate of evolution of albuminoid ammonia in the measures of distillate successively collected will be found in Appendix D. It will be seen that in a very large proportion of the cases before him Dr. Smart has interpreted correctly the general character of the water as to putrescence or comparative freshness of condition of the organic matter. Examples, however, of erroneous results from this principle of interpretation are furnished by Nos. 77, 92, 93, 94, 125, 128, and 131, nearly all of which, it may be observed, were very dilute liquids, and perhaps by the waters (Nos. 113, 114, 116, 117, and 118), containing mixed sewage from Richmond and Washington, though these, also quite dilute, can hardly be quoted as examples involving a known degree of putrescence on the part of the organic matter.

Biological results in connection with putrescent or non-putrescent character of organic matter in water.

On the whole, the biological results obtained, taken in connection with the history and condition of the water samples in which the nature of the organic matter was known, are in accordance with the general belief that putrescent organic matter is more dangerous than that in a fresh or but slowly decomposing condition. Taking the twenty waters which have been noticed above, as containing the most obviously foul, evil smelling, and actively putrescent material, in some of vegetable, in others of animal origin, and comparing these with the lists of waters, as classified by Professor Martin and Dr. Hartwell, we find nine classed as "dangerous," and seven as "suspicious"; of the remaining four, the fact that two represented the weakest dilutions of materials, which in stronger solutions produced marked pathological effects, deserves to be noticed.

GENERAL CONCLUSIONS, WITH A VIEW TO SANITARY APPLICATION, AS TO THE VALUE, SEPARATELY AND COLLECTIVELY, OF THE DIFFERENT PROCESSES OF WATER ANALYSIS WHICH HAVE BEEN UNDER EXAMINATION.

1. It is not possible to decide absolutely upon the wholesomeness or unwholesomeness of a drinking water by the mere use of any of the processes examined for the estimation of *organic matter*, or its constituents.

2. I would even go further, and say that, in judging the sanitary character of a water, not only must such processes be used in connection with the investigation of other evidence of a more general sort, as to the source and history of the water, but should even be deemed of secondary importance in weighing the reasons for accepting or rejecting a water not manifestly unfit for drinking on other grounds.[1]

3. There are no sound grounds on which to establish such general "standards of purity," as have been proposed, looking to

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[1] It will not do merely to throw all doubts on the side of the rejection of a water, as has been more or less advocated by writers on water analysis, for there are often interests of too serious character involved in such rejection to admit of its being decided on, save upon really convincing evidence of its necessity. In view of the great and increasing difficulty of securing an adequate supply of water of satisfactory character for very large cities, is it an unpractical fancy that there may yet come to be provided a double supply through separate pipes: 1st, of water for drinking and cooking purposes only; and 2d, of water less carefully selected as to source and storage for bathing, washing, house and street cleaning, extinguishing fires, &c., the former at any rate dispersed through meters to regulate consumption?

exact amounts of organic carbon or nitrogen, "albuminoid ammonia," oxygen of permanganate consumed, &c., as permissible or not. Distinctions drawn by the application of such standards are arbitrary, and may be misleading.

4. Two entirely legitimate directions seem to be open for the useful examination by chemical means of the organic constituents of drinking water, namely, first, the detection of *very gross* pollution, such as the contamination of the water of a well by accidental bursting or crushing of soil-pipes, extensive leakage of drains,[1] &c., and secondly, the periodical examination of a water supply, as of a great city, in order that, the normal or usual character of the water having been previously ascertained, any suspicious changes which from time to time may occur shall be promptly detected and their cause investigated.

5. In connection with this latter application of water analysis, there seems to be no objection to the establishment of *local* "standards of purity" for drinking water, based on sufficiently thorough examination of the water supply in its usual condition.

6. With the facts of this investigation before me, I am inclined to attach special and very great importance to a careful determination of the nitrites and nitrates in water to be used for drinking.

7. If I had intrusted to me the charge of watching a large city water supply I should use all three of the principal processes for the examination of the organic matter present; each gives a certain amount of information which the others do not afford.

Under circumstances admitting only of the use of simpler means of investigation, the albuminoid ammonia and permanganate processes might be employed together, but in no case should one only of these methods be resorted to, such a course entailing practically the neglect of carbon on the one hand or nitrogen on the other.

PRACTICAL SUGGESTIONS, DRAWN FROM THE EXPERIENCE OF THE INVESTIGATION NOW REPORTED ON, AS TO THE USE IN THEIR PRESENT FORM OF THE CHEMICAL PROCESSES STUDIED.

Examination of water samples in general.

1. Great care should be taken that water samples be placed in the hands of the analyst and their examination begun with the

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[1] Dr. J. S. Billings, U. S. A., of the National Board of Health, has suggested to me in conversation a useful subject of inquiry, viz. the possibility of tracing up the passage of polluting material through a soil by leaching samples of the soil itself, taken at various distances from the source of pollution, or from the water likely to be affected, and chemically examining the liquids obtained.

least possible delay after they have been collected. The changes which take place, sometimes rapidly, on keeping, may seriously affect the results, especially in the case of waters much polluted by foul organic matter.

2. It is very desirable that, besides examining a water in its perfectly fresh condition, samples of it should be set aside, in half-filled but closed glass-stoppered bottles, for some time—say 10 or 12 days—and one of these examined every day or two, so as to trace the character and extent of the changes undergone. Not only may conclusions be drawn from such a series of observations as to the general stability or decomposibility of the organic matter present, but light will be thrown upon the changes which may be expected to occur under ordinary conditions when the water is stored for use, as in cisterns, wells during periods of drought, or carelessly allowed to remain stagnant in pitchers, water-coolers, &c.

Combustion process.

1. In applying this process, no matter how skilful or well trained the analyst may be, duplicate or even triplicate concordant results should be insisted upon before accepting the determinations as trustworthy.

2. In order to avoid the presence in the atmosphere, about the water-bath used for the evaporation, of ammonia derived from coal-gas, the bath should be heated by steam brought in a small, closed pipe from a distant boiler, preferably situated in another room, and the waste steam and condensed water therefrom should be in like manner carried off to a safe distance.

Albuminoid-ammonia process.

1. In order to avoid the uncertain ending of the collection of ammonia, whether "free" or "albuminoid," it would be well to adopt the rule that the distillation be stopped when, and not before, the last measure of distillate collected contains less than a *certain proportion*—say 1 per cent.—of the whole quantity of ammonia already collected. This would in many cases involve the necessity of replenishing the liquid contents of the retort with ammonia-free water.

2. In order to diminish the loss of amines or other volatile forms of nitrogenous matter, a separate distillation should be made with alkaline permanganate added *at once*, in addition to the usual

course of treatment prescribed by Wanklyn—distillation begun with sodium carbonate, and continued after addition of the alkaline permanganate. The results of the two separate distillations should then be compared.

3. In reporting the results obtained by the albuminoid-ammonia process, including the determination of free ammonia, the details of the evolution of ammonia, as collected by separate measures of distillate, should always be given.

Permanganate process.

1. In view of the evidence obtained rendering probable the loss of organic matter by volatilization in the use of acidified permanganate at a boiling temperature, the Tidy form of the process is rather to be recommended than that of Kubel if but one be used.

2. On the other hand, the advantage of more extended oxidizing action, and the greater *general* accordance of the results by the Kubel process with those for organic carbon by the combustion process, make it desirable that as far as possible the same advantages should be secured by substituting the influence of time for that of temperature, and that the time during which the permanganate is allowed to act in the Tidy process should be increased to at least 12, better to 24 hours, *several* determinations (on different samples set aside at the same time) being made at such intermediate intervals as 1, 3, 6, 9, and 12 hours, in order to trace the progress of the oxidation.

SUGGESTIONS AS TO POSSIBLE IMPROVEMENTS ON THE PROCESSES EXAMINED DESERVING FURTHER INVESTIGATION.

Combustion process.

I would propose to evaporate the water, not under ordinary pressure and in contact with the atmosphere, as usual, but as the specimens of water were evaporated for the biological experiments, in a closed vessel immersed in a water-bath and connected with a good (water jet) air pump, so as to secure a nearly complete removal of air, with a condensing worm to dispose in part of the aqueous vapor given off. It would not do to simply place the water in a flask, since the residue could not be removed for combustion, but it would not be difficult to arrange a suitable vacuum vessel, with wide mouth and tightly clamped on cover, within which might be placed the usual glass dish to receive the water, and the feed might be managed through a nearly capillary tube with a glass stop-cock. By such an arrangement the evaporation might be effected within a moderate time at a fixed temperature much lower than the boiling point, thus probably reducing any loss from simple volatilization of organic matter; the nearly complete exclusion of air would tend to greatly diminish or do away with loss of organic matter by oxidation, and permit of large reduction in the quantity of sulphurous acid used; for the same reason the tendency to formation of sulphuric acid would be reduced to a minimum, and the absorption of ammonia from the atmosphere about the dish would be altogether prevented. In testing this last-named effect, two bulb-tubes containing pure sulphuric acid might be interposed between the vacuum chamber and the pump; the contents of the one to be tested for ammonia given off from the water, those of the other to guard against any trace of ammonia coming back from the outside air during irregular action of the stream of water.

2. In order to avoid loss during the evaporation of readily volatile substances, such as butyric, valerianic, &c., acids, to dispense with the necessity for the uncertain and unsatisfactory correction for ammonia lost by dissociation, to get rid of the influence on the determination of organic nitrogen of any errors in the determination of the total ammonia, and to avoid corresponding difficulties arising from the presence of nitrates if these be allowed to remain, it might be well to evaporate at first with the addition of a small excess of magnesia (as recommended by Lechartier), thus removing all ammonia, and then, the water having been brought down to a small volume, add a moderate excess only of sulphurous acid[1] with a drop of a solution of a ferrous salt (as directed by Frankland), and complete the evaporation to dryness—the whole process to be carried out in a jet-pump vacuum, as above suggested.

3. Further experiments are desirable in order to completely determine the merits and defects of the Williams ("copper-zinc couple") method for the removal of nitrates.

4. Some preliminary experiments of my own have seemed to show that nitrates and nitrites may be completely reduced by evaporating to a small bulk with no great excess of phosphorous

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[1] I doubt, however, the possibility of fully reducing nitrates, by means of sulphurous acid, if they are present in large quantity.

or hypo-phosphorous acid, guarding against the evolution of phosphuretted hydrogen by the low temperature employed, then adding magnesia in small excess and completing the evaporation, thus leaving the residue in a pulverulent instead of sticky condition, easy of removal from the dish, and probably allowing of complete combustion without inconvenience from the final oxidation of the small excess of phosphite or hypophosphite, and without any wrapping up of carbon particles. This plan deserves to be carefully tested.

Albuminoid-ammonia process, including determination of free ammonia.

1. In order to prevent, or at least to largely reduce and render uniform, the loss of ammonia from imperfect condensation, I would prefer to effect the distillation, not by a lamp-flame, but in a retort of uniformly determined shape and size, uniformly immersed in a bath of saline solution or other suitable material kept at a uniform temperature—say 102° or 105° C.—by means of steam, and to condense in a glass worm, surrounded by ice-water, sufficiently long to bring the distillate to a uniform temperature, not exceeding, say 5° C.

2. It would be perhaps still better to conduct the distillation in a completely closed apparatus, with a fixed difference of temperature between the retort and the far end of the fully effective condensing tube, with a glass stop-cock to draw off the distillate in successive measured portions, and a little safety-valve (mercury or other) near the cold end to prevent any dangerous difference of external and internal pressure.

3. In the determination of *free* ammonia, with a view to distinguishing as sharply as possible between ammonia really existing as such or in ammoniacal salts and that formed by breaking up of organic matter, it might be well to try a closed distilling apparatus connected with a (water-jet) air-pump, so as to maintain a partial vacuum within, keeping the retort at a fixed temperature much below 100° C., and collecting the whole of the ammonia in a flask and one or more bulb tubes containing rather weak mineral acid, interposed between the condenser and the pump. This would, however, be attended with the disadvantage of not readily permitting the progress of the evolution of ammonia to be traced by its collection in separate successive measures of distillate; and it would become necessary to ascertain whether the application of the

Nessler test would be in any way interfered with by the sodium salts formed from the acid used to collect the ammonia.

4. In order to overcome, if possible, the most serious difficulty in the way of a correct determination of free ammonia, namely, the ready breaking up of urea (and other amides), when present, on heating with sodium carbonate, it would be well to ascertain at how low a temperature and within what time, if at all, ammonia really existing in ammoniacal salts could be completely driven off from an *extremely dilute* solution by adding a small excess of magnesia and maintaining a (water-jet) air-pump vacuum above the liquid, forming a stratum of small depth, with bulb-tubes of acid between the liquid and the pump to intercept the ammonia, and guard-tubes to prevent any being received from the air; in other words, to ascertain whether Schlœsing's method for the determination of ammonia admits of being applied to such excessively minute amounts of it as the water analyst is concerned with.

5. In the conduct of the albuminoid-ammonia process proper, *i. e.* the distillation with alkaline permanganate, I would propose that the original volume of liquid in the retort be maintained *constant*, by running in at the proper rate, through a nearly capillary tube with a glass stop-cock, ammonia-free distilled water. And, in cases in which the amount of organic matter is so large as to wholly, or in great part, reduce the usual charge of alkaline permanganate, I would determine by a preliminary experiment at about what rate the reagent is used up, and would then progressively supply its solution, instead of simply pure water, at such a rate as to keep the original strength as nearly as possible unaltered.

Permanganate process.

1. The principle involved in the last paragraph applies also to this process. Instead of using a fixed amount of permanganate at first, and adding a second or third charge only when the former has been completely reduced, there ought to be a fixed excess at the end of the action, or rather there should be present a constant excess all through the process. Hence, when a preliminary experiment has shown that more than the usual charge of permanganate will be needed, and about the rate at which it will be consumed, for the final experiment additional permanganate solution should be gradually dripped in, from a nearly capillary tube, at such a rate as to maintain the original excess as nearly as possible constant.

2. It is desirable that the process be carried on at a pretty nearly fixed temperature.[1] If the Tidy method be followed, a temperature of say 20° C. could, with a little management, generally be secured, and the flasks kept approximately at this point during the time required for the action.

SUGGESTIONS AS TO FURTHER INVESTIGATIONS IN GENERAL CONNECTION WITH THE SUBJECT-MATTER OF THIS REPORT.

1. It is much to be wished that more extended biological experiments should be made upon the effects of water variously polluted on the lower animals, and that in such experiments the action of water introduced into the stomach as well as hypodermically injected should be tested, and other animals (such as dogs) used as well as rabbits.

2. It would be well to have chemical examinations, on a strictly uniform plan, from time to time made of the water supply in a few of the largest cities at periods when, not mortuary statistics, but the general assent of well-informed members of the medical profession, ascertained through local sanitary authorities, indicates unusual prevalence of, or unusual exemption from, the classes of disease most probably capable of origination from the organic pollution of drinking water.

3. I would *especially* suggest a combined chemical and biological inquiry as to the possible effects upon living animals of the ferment or ferments of nitrification in different stages of that process. In connection with this some minor questions connected with the development of nitrites and nitrates from decomposing organic matter are pointed to, by facts observed in the course of the investigation now reported on, as deserving further examination.

CONCLUSION.—ACKNOWLEDGMENT OF ASSISTANCE RECEIVED.

It remains only for me to record my thanks to the following gentlemen for aid of various kinds, obligingly rendered in connection with the work which forms the subject of this report:

To Prof. H. Newell Martin, of the Johns Hopkins University, for his kind consent to take charge of the biological part of the investigation.

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[1] For experiments on the varying extent of action of permanganate upon organic matter in water at different temperatures, see Bericht. d. deutsch. chem. Gesellsch., **14**, 1015.

To Dr. Chas. Smart, U. S. A., Dr. J. A. Tanner, U. S. N., and Mr. W. A. Noyes, Graduate Scholar of the Johns Hopkins University, for the zeal, care, and patience with which they carried out the actual chemical examination of the waters.

To Dr. E. M. Hartwell, Fellow of the Johns Hopkins University, for like valuable aid in the conduct of the biological work.

To Prof. Ira Remsen, President D. C. Gilman, and the trustees of the Johns Hopkins University, for facilities kindly afforded for the portion of the work carried out in the laboratories of that institution.

To Prof. Wm. Ripley Nichols, of the Massachusetts Institute of Technology, Mr. John E. Hardman, Lake George, N. B., and Mr. W. W. McFarlane, Montreal, Canada, for valuable information as to their experience in using the combustion process.

To Dr. S. M. Bemiss, of the National Board of Health, New Orleans, La.; Dr. Allard Memminger, Charleston, S. C.; Dr. H. B. Horlbeck, Charleston, S. C.; Prof. Gaetano Lanza, of the Massachusetts Institute of Technology; Mr. M. Benjamin, New York; Messrs. Jas. W. Queen & Co., Philadelphia; Dr. J. G. Cabell, Richmond, Va.; Prof. M. Delafontaine, Chicago, Ill.; Dr. E. D. Coonley, Mariner's Harbor, Staten Island, N. Y.; Mr. Thos. L. Hobart, Titusville, Pa.; Mr. H. V. Strayer, Harrisonburg, Va.; Dr. Geo. M. Ockford, Burlington, Vt.; Dr. R. W. Dorsey, Fairfax Court-House, Va.; Dr. M. B. Harris, Andover, Mass.; Dr. G. G. Craig, Rock Island, Ill.; Dr. J. A. Dibrell, jr., Little Rock, Ark.; Dr. John McCarrell, Wellsville, Ohio; Mr. Chas. P. Peterman, Mt. Vernon, Ohio; Dr. H. M. Warren, Jonesville, Mich.; Dr. Wm. H. Johnson, Adamstown, Md.; Dr. W. H. Rand, Charlotte, Mich.; Dr. C. Drew, jr., Jacksonville, Fla.; Dr. Henry Mitchell, Asbury Park, N. J.; Dr. A. B. Brumbaugh, Huntingdon, Pa.; Dr. M. J. Lowry, Meridian, Miss.; Dr. A. M. Oldfield, Lexington, Mich.; Mr. M. O. West, Port Chester, N. Y.; Mr. F. C. Tomlinson, Closter, N. J.; Dr. W. D. Carter, Ripley, Miss.; Dr. S. T. Evans, Union City, Tenn.; Dr. H. J. Cate, Poughkeepsie, N. Y.; Dr. J. L. Carter, Dallas, Tex.; Dr. H. H. Longstreet, Bordentown, N. J.; Prof. Raphael Pumpelly, Newport, R. I.; Dr. Geo. A. Smyth, Newport, R. I.; Dr. John L. Nelson, U. S. Flagship New Hampshire; Dr. Horatio R. Storer, Newport, R. I.; and Mr. E. A. Hatton, Portsmouth, Va., for assistance in procuring samples of natural waters.

To Mr. Z. Davis, Charleston, S. C.; Dr. S. H. Moffett, Harrisonburg, Va.; Dr. W. D. Hopkins, Harrisonburg, Va.; Dr. D. H. Dungan, Little Rock, Ark.; Dr. E. F. Mathews, Port Chester, N. Y.; Dr. H. A. Crary, Closter, N. J.; and Mr. W. C. Connor, Dallas, Tex., for information in regard to some of the water samples examined.

To Mr. Chas. E. Heald, Lynchburg, Va.; The Montague Paper Company, Turner's Falls, Mass.; Mr. Wright Duryea, New York; Mr. T. A. Havemeyer, New York; Mr. P. Casamajor, New York; Dr. H. H. Longstreet, Bordentown, N. J.; Mr. H. C. Marchant, Charlottesville, Va.; and Mr. J. C. Hewitt, New York, for specimens of factory refuse of various kinds.

To Dr. W. C. Dabney, Charlottesville, Va.; Dr. F. P. Porcher and Dr. Allard Memminger, Charleston, S. C.; and Dr. D. M. Burgess, Havana, Cuba, for specimens of morbid material; and to a large number of other gentlemen in various parts of the country, who offered samples of suspected waters for examination, the evidence against which, however, did not appear sufficient to make them available for the purpose of the investigation in hand.

MINERALS FROM FRITZ ISLAND, PA.

By Benj. Sadtler, Jr.

Finding that no analyses of the chabazites and mesolites of this State had been made, and having some good specimens at my command, I have analyzed both minerals. The specimens used came from Fritz Island, near Reading, Pa., where they are found associated with thomsonite, apophyllite, calcite, and, more rarely, an undescribed zeolite which has been analyzed by Dr. Genth (Mineralogy of Penna., page 110.)

1. The chabazite occurs in well-developed rhombohedral crystals, rarely modified by other rhombic forms. The crystals are colorless and of a vitreous lustre, having a hardness of 4, and sp. gr. 2.3. An analysis gave the following results:

H_2O	20.21
SiO_2	50.28
Al_2O_3	17.83

CaO	6.96
Na_2O	2.43
K_2O	2.40
Fe_2O_3	trace
MgO	.22
	100.33

2. The mesolite is found in globular concretions or tufts of fine white fibres. Hardness 2.5—3, and sp. gr. 2.4. After determining and allowing for a very slight amount (about one-fifth of a per cent.) of calcite, from which it was impossible to entirely free the mineral, the analysis was as follows:

H_2O	16.01
SiO_2	43.29
Fe_2O_3	trace
Al_2O_3	25.02
CaO	12.15
Na_2O	3.40
	99.87

3. I also made an analysis of the apophyllite from the same locality. It occurred in tetragonal tablets modified by octahedral planes. The crystals were colorless and of a pearly lustre. Hardness 4—4.5, sp. gr. 2.5. Appended is the analysis:

H_2O	16.75
SiO_2	51.02
Fe_2O_3	1.49
CaO	24.40
K_2O	5.87
Fl	.40
	99.93

Muhlenberg College, Allentown, Pa., Nov. 15th, 1882.

MANGANESE BORATE.

By N. Wiley Thomas.

In a recent article[1] published by Smith, upon the determination of boracic acid, a precipitate was obtained to which the formula MnB_4O_7 was assigned. I have since been requested to examine this compound, and append my results.

The salt was obtained by precipitating 10 cc. borax solution (containing .1000 gram $Na_2B_4O_7 + 10H_2O$) with 10 cc. manganese sulphate (.0600 gram $MnSO_4$) in presence of alcohol. After the precipitate had completely subsided, it was rapidly filtered and washed with alcohol. The alcoholic filtrate was evaporated, and the excess of manganese sulphate determined with a solution of potassium permanganate, 1 cc. of which $=$ .0045 gram $MnSO_4$. The excess required 4.6 cc. $KMnO_4$, corresponding to .0207 gram $MnSO_4$.

The manganese borate after washing was dissolved in sulphuric acid and evaporated to dryness several times, the residual manganese sulphate dissolved in water, zinc sulphate added, heat applied, and potassium permanganate run in until a permanent pink color was imparted to the liquid. The $KMnO_4$ used was 8.6 cc., corresponding to .0387 gram $MnSO_4 =$ .0180 gram MnO. The 10 cc. manganese sulphate contained .0600 gram. The excess of $MnSO_4$ in the filtrate determined by $KMnO_4 =$ .0207. The quantity of manganese sulphate then reacting with 10 cc. $Na_2B_4O_7 =$ .0600 —.0207 or .0393 $MnSO_4$, and by actual determination I found .0387 gram.

.0393 gram $MnSO_4 =$ .0183 gram MnO.
.0387 " " $=$ .0180 " "

In the borax solution (0.1000 gram borax) there is .0366 gram boron trioxide, and this would require .0183 gram MnO for union. As already noticed above, I found by actual determination .0180 gram MnO in the borate. Upon comparing the amounts of boron trioxide and manganous oxide found, we have:

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[1] This Journal **4**, 279.

.0180 gram MnO $\div$ 70 $=$ 25 $\div$ 25 $=$ 1 mol. MnO
.0366 " " $\div$ 70 $=$ 50 $\div$ 25 $=$ 2 mol. B_2O_3

or the formula would be MnB_4O_7, as written.

A second determination gave the following:

In this case the salt was obtained by precipitating 5 cc. borax solution (same strength as preceding) with 5 cc. manganese sulphate (also previous strength) in the presence of alcohol. The operation was carried out as in the first case. The required $KMnO_4$ was 4.3 cc., corresponding to .0194 gram $MnSO_4$ $=$ .0090 MnO. The 5 cc. manganese sulphate contained .0300 gram. The excess of $MnSO_4$ in the filtrate determined by $KMnO_4$ $=$ .0104 gram. The quantity of manganese sulphate then reacting with the 5 cc. borax solution equalled .0300 — .0104 $=$ .0196 gram. By analysis I found .0193 gram. These results lead to the same formula for the borate as those above.

DETERMINATION OF IRON IN HYDROCHLORIC ACID SOLUTIONS BY POTASSIUM PERMANGANATE.

By N. Wiley Thomas.

Zimmerman has described[1] a modification of Margueritte's method for determining iron in presence of hydrochloric acid, and finds that manganous sulphate prevents the chlorine from acting upon the permanganate, while nickel, cobalt and copper salts are worthless. It appears not amiss to mention that in this laboratory we have employed a solution of lead chloride for the same purpose that Zimmerman uses manganous sulphate, and find upon comparing results with those in which the manganese salt has been used, that they agree remarkably well. As they may be of interest to chemists I record them here, and also give analyses in which only sulphuric acid was present, with several in which manganous sulphate was employed.

The solutions used were of the following concentrations: $MnSO_4$ $=$ 100 grams in 200 cc. H_2O, HCl $=$ 1.1398 sp. gr. and 1.20, $PbCl_2$

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[1] Annalen der Chemie, **213**, 307.

$=5$ grams in 100 cc. H_2O. 1 cc. of the $KMnO_4$ solution equalled .00528 gram metallic Fe.

Iron Solution. cc.	H_2O. cc.	HCl. cc.	$PbCl_2$. cc.	$MnSO_4$. cc.	H_2SO_4. cc.	$KMnO_4$. cc.
1......50	300	...	...	...	20	27.6
2......50	300	...	...	...	20	27.6
3......50	300	35	...	10	...	27.6
4......50	300	20	...	10	...	27.6
5......50	400	35	...	10	...	27.6
6......50	400	20	10	...	...	27.6
7......50	400	30	10	...	...	27.6
8......50	400	20	10	...	...	27.6
9......50	400	20	10	...	...	27.6
10......50	400	20	10	...	...	27.6
11......50	400	20	10	...	...	27.6
12......50	400	20	10	...	...	27.6

Muhlenberg College, Allentown, Pa., Nov. 11, 1882.

Contributions from the Chemical Laboratory of Harvard College.

XXVII.—ON CERTAIN SUBSTANCES OBTAINED FROM TURMERIC.—CURCUMIN.[1]

By C. Loring Jackson and A. E. Menke.

The following paper[2] contains a description of our experiments on the action of nascent hydrogen and of bromine upon curcumin.

Action of Nascent Hydrogen.

Dihydride of Curcumin, $C_{14}H_{16}O_4$.—This substance was made by the action of sodium amalgam and water upon curcumin. The best result was obtained when a mixture of curcumin, dilute alcohol, and strong sodium amalgam was allowed to stand for somewhat more than a week. The alcohol, though not absolutely necessary, as the sodic hydrate formed gradually brings the curcumin into solution, accelerates the action, which at best is extremely slow. After the dark-red color of the sodic salt of curcumin had given place to a blackish tinge, the liquid was poured off from the mercury, acidified with hydrochloric acid, the fawn-colored precipitate thus obtained washed till free from acid, and dried *in vacuo.* A combustion gave the following results:

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[1] From the Proceedings of the American Academy of Arts and Sciences. Communicated by the authors.

[2] The first paper was published in this Journal **4**, 77.

0.2290 gram of substance gave 0.5678 gram of CO_2 and 0.1312 gram of H_2O.

	Calculated for $C_{14}H_{16}O_4$.	Found.
Carbon	67.74	67.63
Hydrogen	6.49	6.36

Properties.—It forms a brownish-white powder melting in the neighborhood of 100°, but with no definite melting point; it is insoluble in water, freely soluble in alcohol and glacial acetic acid, slightly in ether, and insoluble in ligroine and benzol. Strong sulphuric acid dissolves it with a reddish-brown color, very different from the purple produced by curcumin. Sodic hydrate dissolves it on warming, and so does sodic carbonate; but the latter solution becomes turbid, and throws down a brownish precipitate on cooling.

The addition of hydrogen to curcumin by sodium amalgam and dilute alcohol is a tedious process, occupying more than a week and giving a very bad yield, the product being frequently accompanied by a viscous substance, probably formed by the action of air on the alkaline solution of the hydride. A much better method of adding hydrogen to curcumin consisted in treating it with zinc dust and acetic acid, although in this case the hydride at first produced was further modified in the course of the reaction.

Anhydride of Curcumin Dihydride, $(C_{14}H_{15}O_4)_2O$.—Curcumin was warmed with acetic acid of 85 per cent. and a large quantity of zinc dust, the temperature being kept below the boiling point of the acetic acid. After some hours the yellow color of the solution had become replaced by a dark brown, and if then a little of the substance gave a yellow instead of a red color with sodic hydrate, the heating was discontinued, and the liquid filtered into water, which precipitated fawn-colored flocks similar to those of the preceding compound. After we had satisfied ourselves that it was impossible to crystallize the substance, we purified it by resolution in glacial acetic acid and precipitation with water; but even this treatment did not remove the whole of the zinc salt, as was shown by the appearance of a slight ash on combustion. This has been subtracted from the weight of the substance taken in calculating the percentages.

The same substance was obtained when curcumin was heated with zinc dust and a solution of ammonic hydrate. The combustion marked III was of a product made in this way:

The substance after thorough washing with water was in each case dried on a steam radiator at a temperature of about 60°.

I. 0.2552 gram of substance gave 0.6460 gram of CO_2. 0.1476 gram of H_2O. Ash = 0.004.

II. 0.2449 gram of substance gave 0.6183 gram of CO_2. 0.1368 gram of H_2O. Ash = 0.0061.

III. 0.2357 gram of substance gave 0.6001 gram of CO_2. 0.1365 gram of H_2O. Ash = 0.002.

	Calculated for $C_{28}H_{30}O_7$.	Found.		
		I.	II.	III.
Carbon	70.42	70.14[1]	70.61[1]	70.03[1]
Hydrogen	6.25	6.53	6.36	6.48

Properties.—It resembles the dihydride closely, like it forming a dirty white powder, with no definite melting point, since it melts gradually in the neighborhood of 120°. The best solvents for it are alcohol and glacial acetic acid, but it is deposited on evaporation of the solvent as a varnish. It is essentially insoluble in ether, ligroine, and benzol, slightly soluble in chloroform. A solution of potassic hydrate dissolves it with a yellow color, while potassic carbonate forms a dark-brown solution if boiled with it, but as this solution cools, brownish flocks are deposited, which we supposed to be a potassium salt, until two analyses of the substance showed that it did not contain more than 2.5 per cent. of potassium, whereas the salt with the least possible amount of the metal contains 7.5 per cent. It is evident, therefore, that the potassium was an impurity, which could well be, since we were able to find no satisfactory method of purification. An attempt to make a potassium salt with alcoholic potassic hydrate gave a black liquid, insoluble in a mixture of alcohol and ether, and of the most unpromising appearance.

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[1] If the ash is not subtracted the percentages are—

I.	II.	III.
69.04	68.85	60.44
6.43	6.20	6.43

The fact that the substance forms no salt with potassic carbonate indicates that the two molecules of the dihydride are connected by the removal of water from their carboxyl groups; but we did not consider the nature of the substance satisfactorily explained until we succeeded in making it from the dihydride, $C_{14}H_{16}O_4$, by the action of an acetic acid solution of zincic acetate. After warming the two substances together for some time, the product was treated with water, and the precipitate washed, dried, and analyzed, with the following result:

0.1430 gram of substance gave 0.3666 gram of CO_2 and 0.0868 gram H_2O.

	Calculated for $C_{28}H_{30}O_7$.	Found.
Carbon	70.42	69.92
Hydrogen	6.25	6.68

Whereas before this treatment a portion of the same sample gave carbon 67.63, hydrogen 6.36, as on page 361. This experiment proves, therefore, that the nascent hydrogen given off by zinc dust and acetic acid first converts the curcumin into the dihydride, from which the zincic acetate afterward removes one molecule of water. The anhydride is broken up only incompletely by the action of water at high temperatures or by boiling with sodic hydrate, the product in each case being a mixture of the dihydride and its anhydride.

In order to study the oxidation of the dihydride, some diethylcurcumin, prepared according to the method given in our first paper, was treated with zinc dust and acetic acid. The product thus obtained gave the following results on analysis, which indicate that it is a mixture of di- and monoethylcurcumin dihydride:

I. 0.2130 gram of substance gave 0.5484 gram of CO_2 and 0.1415 gram of H_2O. Ash 0.0004.

II. 0.1938 gram of substance gave 0.4986 gram of CO_2 and 0.1336 gram of H_2O.

	Calculated for $(C_2H_5)C_{14}H_{15}O_4$.	Found.		Calculated for $(C_2H_5)_2C_{14}H_{15}O_4$.
		I.	II.	
Carbon	69.59	70.35	70.15	71.05
Hydrogen	7.25	7.40	7.66	7.89

Some of this substance was mixed with a satuated neutral solution of potassic permanganate and allowed to stand at the ordinary temperature. The oxidation took place very slowly, several weeks' standing being necessary to complete the reaction. The principal product was proved by its melting point to be ethylvanillic acid, while the presence of a small quantity of ethylvanillin was indicated by its characteristic smell.

The most striking fact in connection with this reaction was that the dihydride was oxidized with much more difficulty than curcumin itself.

Action of Bromine on the Anhydride of Curcumin Dihydride. When the hydride, dissolved in glacial acetic acid, was mixed with an excess of bromine and allowed to stand over night, the liquid turned black, and upon addition of water, a red percipitate was thrown down, which was washed with water, dried, and analyzed:

I. 0.6652 gram of substance gave 0.7160 gram of CO_2 and 0.1122 gram of H_2O. 0.3100 gram gave according to Carius 0.4125 gram of AgBr.

II. 0.3202 gram gave 0.3498 gram of CO_2 and 0.0562 gram of H_2O. 0.2786 gram gave 0.3730 gram of AgBr.

	Calculated for $C_{14}H_{10}Br_4O_4$.	Found.	
		I.	II.
Carbon	29.89	29.36	29.80
Hydrogen	1.78	1.87	1.95
Bromine	56.94	56.62	56.99

The substance is red and amorphous; it does not melt under a red heat, but seems to be decomposed without melting. It is insoluble in water, ligroine, and benzol, very slightly soluble in alcohol and ether, soluble in glacial acetic acid. Strong sulphuric acid has no action upon it. It is vigorously acted on by boiling potassic hydrate, forming a red solution, from which acids precipitate a black tarry body which we were unable to purify; two analyses of its sodium salt, however, showed that it contained about the same percentage of oxygen as of carbon, and that most of the bromine (all but 7 per cent.) had been removed, proving that the bromine in the original substance is all in the side-chain.

Action of Bromine on Curcumin.

We have obtained two bromine compounds of curcumin, one containing four and the other seven atoms of bromine.

Tetrabromide of Curcumin, $C_{14}H_{14}Br_4O_4$.—When curcumin suspended in carbonic disulphide is allowed to stand with an excess of bromine for some hours, it is converted into a white substance, which is left as the carbonic disulphide evaporates. The carbonic disulphide can be replaced by glacial acetic acid, but in this case an excess of bromine or the use of a large quantity of glacial acetic acid must be avoided. The nature of this body could not be established satisfactorily by analysis, as it was more or less decomposed by all its solvents, and therefore a thorough purification was impossible; we have obtained one fair analysis, however, of a sample washed with carbonic disulphide.

0.2375 gram of substance gave according to Carius 0.3180 gram of AgBr.

	Calculated for $C_{14}H_{14}Br_4O_4$.	Found.
Bromine	56.66	56.99

Other specimens contained the following percentages:

Bromine	54.87	58.51	58.57

To confirm this result, which points to the taking up of four atoms of bromine, we determined the increase of weight caused by the bromine. For this purpose carbonic disulphide and bromine in excess were added to a weighed amount of curcumin, and the product weighed after drying it a little below 100°.

I. 0.252 gram of curcumin gained 0.354 gram.

II. 0.218 gram gained 0.300 gram.

These results correspond to the following percentages of bromine in the product,—

	Calculated for $C_{14}H_{14}Br_4O_4$.	Found.	
		I.	II.
Bromine	56.66	58.41	57.91

And there is therefore no doubt that the substance contains four atoms of bromine. To decide whether it was an addition or substitution product, we determined the amount of hydrobromic acid given off, as in every preparation an evolution of this gas was observed. For this purpose the gases formed in the reaction were allowed to pass through water, and finally the carbonic disulphide and excess of bromine were removed, at first from the curcumin, and afterward from the absorbing water, by a stream of air; the hydrobromic acid collected in the water was then determined as argentic bromide. One gram of curcumin was used in each case, and in the following comparison of results the amounts found are compared with the calculated amount if the curcumin had given off two molecules of hydrobromic acid,—

Two Molecules HBr.	I.	II.
0.66	0.185	0.28

From this it appears that the hydrobromic acid is produced by an insignificant secondary reaction, and that the substance is an addition product, and therefore has the formula $C_{14}H_{14}Br_4O_4$.[1] We may add that some experiments to determine directly the number of molecules of bromine added pointed to two molecules as the probable amount, but the results are not definite enough to make them worth publishing.

Properties.—It is a white or whitish amorphous substance, melting in the neighborhood of 185° with decomposition, but it has no definite melting point. It is insoluble in water, soluble with decomposition in alcohol and in glacial acetic acid, which acts upon it, however, less rapidly than the alcohol, very slightly soluble in ether, chloroform, and carbonic disulphide, insoluble in ligroine and benzol. Its behavior with various reagents was taken up, but no results were obtained which promised to repay further study. The following observations, however, are of some interest. Potassic hydrate and also argentic oxide convert it in part into vanillin, to judge from the smell, while both anilin and zinc cleaned with sulphuric acid act upon it, the former with considerable evolution of heat,—thus confirming the inference that it is an addition product. The principal products from these reactions, as well as those from the action of sodic carbonate and water, and of reducing agents, are ill-defined bodies which we could find no means of purifying.

Pentabromcurcumindibromide, $C_{14}H_9Br_7O_4$.—If curcumin in glacial acetic acid is treated with an excess of bromine, or the solid tetrabromide treated with bromine, a red substance is formed, which, after washing with water and drying *in vacuo*, gave the following results :

0.2898 gram of substance gave 0.2230 gram of CO_2 and 0.0304 gram of H_2O.

0.2666 gram of substance gave according to Carius 0.9323 gram of AgBr.

	Calculated for $C_{14}H_9Br_7O_4$.	Found.
Carbon	20.97	20.98
Hydrogen	1.12	1.16
Bromine	69.91	69.02

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[1] The high percentages of bromine obtained in the analyses may be accounted for by this secondary reaction.

Properties.—A red amorphous substance melting near 120°, but without definite melting point; insoluble in water, soluble in alcohol apparently with decomposition, easily soluble in ether and glacial acetic acid, leaving a varnish, slightly soluble in benzol, insoluble in ligroine. Strong sulphuric acid acts on it very slowly, finally turning it a more brilliant red. Our study of the behavior of this substance has led to no more definite results than in the case of the tetrabromide.

Heated alone, it gives off bromine and hydrobromic acid, leaving a black tar, from which a yellow substance containing bromine can be extracted by alcohol; we may study this experiment more carefully hereafter. Sodic hydrate, sodic carbonate and water, sodic alcoholate, and argentic oxide all act upon it, but no smell of vanillin was observed in any case. The same is true of several oxidation experiments we have tried upon it, and this would seem to indicate the presence of a portion of the bromine in the benzol ring. It is an interesting fact that potassic dichromate and sulphuric acid, and also neutral potassic permanganate, attack this substance only with extreme difficulty, whereas they both act vigorously on curcumin.

SUMMARY.

1. Curcumin takes up two atoms of hydrogen when treated with nascent hydrogen.
2. The dihydride thus formed passes over easily into an anhydride by losing one molecule of water.
3. The anhydride of diethylcurcumin dihydride is much less easily attacked by oxidizing agents than diethylcurcumin, but the products are the same,—ethylvanillic acid with a trace of ethylvanillin.
4. Bromine removes two atoms of hydrogen from the dihydride, and replaces four more, forming $C_{14}H_{10}Br_4O_4$.
5. Only four atoms of bromine can be added to curcumin.
6. The tetrabromide has a great tendency to form vanillin when treated with substances which remove bromine.
7. With an excess of bromine a substance, $C_{14}H_9Br_7O_4$, is formed.
8. The pentabromcurcumindibromide is oxidized in neutral or acid solutions only with great difficulty.

The observations just described throw some light upon the nature of the side-chain of curcumin, but as the inferences to be drawn from them are at best extremely doubtful, we shall postpone all discussion of the structure of curcumin until our further study of it has put the subject on a more secure basis.

XXVIII.—TURMERIC OIL.—TURMEROL.

By C. Loring Jackson and A. E. Menke.

The oil obtained from turmeric, which amounts to about 11 per cent. of its whole weight, has naturally attracted the attention of chemists much less than curcumin, the yellow coloring-matter of the root; we find consequently only a few analyses and some meagre statements about the action of reagents upon the oil, in place of the much fuller study to which curcumin had been submitted. The most important of these will be found in the papers of Ivanow-Gajewsky[1] and Kachler,[2] but as they all refer to mixtures, it is not necessary to repeat them here. The oil, however, is not without practical interest, as to it the turmeric (and therefore curry powder) owes its aromatic taste and smell.

The crude product with which we started in the following study of the oil was extracted from ground Bengal tumeric with ligroine, in the way already described in the first paper[3] of this series. After being freed from the higher boiling portions of the ligroine by heating to 150° in a boiling flask, it formed a rather thick oily liquid, with a yellow color and pleasant aromatic smell. The purification offered some difficulty, because it was decomposed by distillation under ordinary pressure, giving distillates with a rank, disagreeable smell; and distillation with steam, although effecting a partial purification, was an extremely tedious process, owing to the difficulty with which the oil was driven over. We were therefore obliged to resort to fractional distillation under diminished pressure, and in this way at last succeeded in separating the oil into three fractions—the first, boiling below 193° under 60 mm. of pressure; the second, from 193°–198°; and the third, the retort residue, a viscous, semi-solid body of extremely uninviting appearance. We have up to this time confined our attention to the middle fraction, although a few experiments on the fraction below 193° would indicate that it consists of the middle fraction contaminated with hydrocarbons from the ligroine used in the extraction of the oil—a view which is borne out by the very small amount of this fraction. For the fraction from 193°–198°, which is the subject of this paper, we would propose the name *turmerol.*

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[1] Berichte der deutschen chemischen Gesellschaft, **172**, 1103.

[2] *Ibid.* **170**, 713.

[3] This Journal, **4**, 77.

Composition of Turmerol.

I. 0.1924 gram of the oil gave 0.5903 gram of CO_2 and 0.1814 gram of H_2O.

II. 0.3126 gram gave 0.9588 gram of CO_2 and 0.3010 gram of H_2O.

III. 0.2354 gram gave 0.7157 gram of CO_2 and 0.2190 gram of H_2O.

IV. 0.2002 gram gave 0.6123 gram of CO_2 and 0.1818 gram of H_2O.

V. 0.2448 gram gave 0.7492 gram of CO_2 and 0.2306 gram of H_2O.

	I.	II.	III.	IV.	V.	Mean.
Carbon	83.68	83.66	82.90	83.43	83.47	83.62
Hydrogen	10.47	10.70	10.34	10.10	10.47	10.42

I–III are analyses of the same sample; IV and V analyses of a different sample. To test the purity of the oil, the original sample was distilled again *in vacuo*, and collected in three equal fractions. Of the analyses which follow, VI was made with the portion which came over first; VII and VIII with that which came over last.

VI. 0.3315 gram gave 1.0194 gram of CO_2 and 0.3145 gram of H_2O.

VII. 0.2837 gram gave 0.8675 gram of CO_2 and 0.2604 gram of H_2O.

VIII. 0.2706 gram gave 0.8228 gram of CO_2 and 0.2474 gram of H_2O.

	Lower Fraction.	Higher Fractions.	
	VI.	VII.	VIII.
Carbon	83.86	83.39	82.92
Hydrogen	10.54	10.20	10.16

From this it appears that the substance is essentially pure and homogeneous.

As has been stated already, the turmerol can be purified to a certain extent by distillation with steam; analysis IX was made with a sample prepared in this way, while X was made with some of the same sample after it had been distilled once under ordinary pressure. These specimens were extracted with carbonic disulphide instead of ligroine.

IX. 0.2260 gram gave 0.6860 gram of CO_2 and 0.2195 gram of H_2O.

X. 0.2636 gram gave 0.8038 gram of CO_2 and 0.2546 gram of H_2O.

	IX.	X.
Carbon	82.78	83.16
Hydrogen	10.77	10.73

The analyses unfortunately are not capable of establishing the formula of turmerol with certainty, since the difference between the members of the homologous series is very small, as is shown by the following comparison:

	Mean of the Preceding Analyses.	$C_{18}H_{26}O$.	$C_{19}H_{28}O$.	$C_{20}H_{30}O$.
Carbon	83.62	83.73	83.81	83.90
Hydrogen	10.42	10.08	10.29	10.49

Taking both the hydrogen and the carbon into consideration, our results agree best with the formula $C_{19}H_{28}O$, as shown above in the case of the mean, and a comparison of the separate analyses with the calculated percentages also declares in favor of this formula. But it is evident that it is impossible to decide definitely from these data in favor of this formula, nor can the derivatives we have prepared from the oil settle this question, as a thorough purification of these bodies has proved impossible on account of their ill-defined properties and slight stability.

We are inclined to ascribe the difference between analyses VI and VII and VIII to the presence of a trace of some hydrocarbon from the ligroine, but did not attempt to purify the substance further, as it is slightly decomposed, even by distillation, under a pressure of 60 mm.

Properties of Turmerol.

The substance analyzed by us had a pale yellow color, an agreeable, not very strong aromatic smell, and a specific gravity of

0.9016 at 17°. It turns a ray of polarized light to the right with the following specific rotary power for sodium light:

$$[\alpha] = 33.52.$$

Under ordinary pressure it boils at 285°–290°, but decomposes apparently with formation of water, giving a substance with a lower boiling point. At a pressure of 60 mm. it boils from 193°–198°, but even under this pressure suffers a slight decomposition. It is essentially insoluble in water, but mixes easily with all other common solvents. Acid sodic sulphite in aqueous solution has no action upon it.

In order to determine the nature of turmerol, its behavior with various reagents was next studied.

Action of Hydrochloric Acid.—Turmerylchloride.

When turmerol was heated with aqueous hydrochloric acid saturated at 0° to 150° in a sealed tube for some hours, a brown oily liquid was formed having a different smell from the original substance, which, when washed until free from acid and dried *in vacuo*, gave the following results on analysis:

I. 0.2938 gram of substance gave 0.8464 gram of CO_2 and 0.2530 gram of H_2O.

0.4434 gram of substance gave according to Carius 0.2190 gram of AgCl.

II. 0.3179 gram of substance gave 0.1518 gram of AgCl.

	Calculated for $C_{19}H_{27}Cl$.	Found.	
		I.	II.
Carbon	78.48	78.57	
Hydrogen	9.30	9.57	
Chloride	12.22	12.21	11.80
	100.00	100.35	

Analyses I and II were made with specimens from different preparations. The substance was a pale brownish oil with an agreeable smell, different from that of turmerol; it decomposed on distillation, and also lost chlorine when distilled with steam or even with fuming hydrochloric acid.

The same compound was formed by the action of phosphorous trichloride on turmerol, but much less neatly. Phosphoric pentachloride, on the other hand, seemed to add chlorine also, as the product from its action on turmerol contained about 15 per cent. of chlorine. We have postponed the study of this substance for the present.

The formation of the turmerylchloride described above indicates that turmerol is an alcohol, and to confirm this view we next treated the turmerylchloride with various reagents, and found that its chlorine was removed, in part, at least, by boiling water or by alcoholic solutions of sodic acetate, potassic cyanide, or ammonia—a substance being formed in each case with the characteristic smell of the class to which it should belong. The regenerated alcohol and the acetate we were unable to purify, while the nitrile and its corresponding acid and the amine were formed in very small quantities and did not give crystalline compounds, so that their further study, which we had at first hoped would establish the formula of turmerol, did not promise to repay the labor.

To still further confirm the alcoholic nature of turmerol, we prepared the sodium compound as follows:

Action of Sodium on Turmerol.

Some of the turmerol mixed with high boiling ligroine was warmed with sodium in a flask with a return cooler for twelve hours, during which time hydrogen was given off; the liquid was then filtered, and the ligroine evaporated off from the viscous filtrate.

I. 0.1456 gram of substance gave 0.0374 gram of Na_2SO_4.
II. 0.9820 gram gave 0.2342 gram of Na_2SO_4.

	Calculated for $C_{19}H_{27}ONa$.	Found. I.	Found. II.
Sodium	7.82	8.32	7.72

The substance forms a viscous semi-solid mass.

Sodic hydrate seemed not to act upon turmerol.

An attempt to convert turmerol into its acetate by heating it with acetic anhydride and sodic acetate on the water-bath gave a product having the same smell as that from the reaction of sodic acetate on turmerylchloride, but no means could be found of separating it from the unaltered turmerol, as it was decomposed by distillation even *in vacuo*. We accordingly turned our attention to the ethers of turmerol, and selected for study the isobutylether, as the difference between the percentage composition of this and that of the alcohol would be greater than in the case of the methyl- or ethylethers.

Isobutylether of Turmerol.

This body was prepared by boiling the sodium compound with isobutyliodide in a flask with a return-condenser for some time; the product was purified by distillation *in vacuo*.

I. 0.2110 gram of substance gave 0.6524 gram of CO_2 and 0.2039 gram of H_2O.

II. 0.2742 gram of substance gave 0.8520 gram of CO_2 and 0.2646 gram of H_2O.

	Calculated for $C_{19}H_{27}OC_4H_9$.	Found.	
		I.	II.
Carbon	84.14	84.45	84.71
Hydrogen	10.97	10.73	10.83

It is a heavy yellowish oil with a pleasant smell. The ethylether is a similar substance.

From the observations described there can be no doubt that turmerol is an alcohol.

Oxidation of Turmerol.

When turmerol was treated with a hot aqueous solution of potassic permanganate until it was no longer decolorized, and after destroying the slight excess of permanganate with sodic sulphite the liquid was filtered from the brown hydrate of manganese, upon adding sulphuric acid a yellowish-white precipitate was thrown down, which, purified by washing with alcohol, became perfectly white, and volatilized without melting, indicating that it was terephthalic acid. To prove that this was the case, the acid was converted into the methylester by passing hydrochloric acid through methylalcohol, in which it was suspended. The solid gradually dissolved, and upon allowing the alcohol to evaporate, long prisms were deposited, which, after two crystallizations from hot alcohol, melted at 139°–140°. Melting point of methylester of terephthalic acid 140°. Another sample of the acid was analyzed:

0.1782 gram of substance gave 0.3798 gram of CO_2 and 0.0641 of H_2O.

	Calculated for $C_8H_6O_4$.	Found.
Carbon	57.83	58.12
Hydrogen	3.62	4.00

The product in this case, therefore, is terephthalic acid, and turmerol must stand in close relationship to the para series of aromatic compounds. It is probably a derivative of the terpenes.

The formation of terephthalic acid from turmeric oil also explains the results of Ivanow-Gajewsky in regard to the oxidation of curcumin, as it renders it almost certain that the terephthalic acid obtained by him, but of which we could find no trace, proceeded from an impurity of turmeric oil in his curcumin.

When cold potassic permanganate not in excess is used, turmerol yields one or more apparently new acids, with the investigation of which we are at present occupied.

SUMMARY.

The formula of turmerol (the fraction of turmeric oil boiling from 193° to 198° under 60 mm. of pressure) is $C_{19}H_{28}O$, or one of its adjacent homologues.

Its alcoholic nature is proved by the following observations:

1. Conversion into $C_{19}H_{27}Cl$ by hydrochloric acid or phosphorous trichloride. The chlorine can be removed by ordinary reagents.

2. The formation of a compound, $C_{19}H_{27}ONa$, by the action of sodium.

3. The formation of its isobutylether, $C_{19}H_{27}OC_4H_9$.

That it is related to the para compounds of the aromatic series is proved by its conversion into terephthalic acid by treatment with a hot aqueous solution of potassic permanganate in excess.

ON ETHOXY-METATOLUIC ACID.

By P. H. Broun.

In a paper[1] recently published, Remsen and Kuhara proved that the nitro-toluic acid obtained by oxidation of ordinary nitro-xylene with chromic acid contains the nitro-group in the ortho-position relatively to the methyl, and in the para-position relatively to the carboxyl. This was shown by converting the nitro-acid into the corresponding hydroxy-acid, which was found to be ortho-homoparoxybenzoic acid $C_6H_3\left\{\begin{array}{ll}OH & (1)\\ CH_3 & (2)\\ COOH & (4)\end{array}\right.$. While the diazo-compound was readily converted into the hydroxy-acid by boiling with water, it was found that, when boiled with alcohol, it did not yield metatoluic acid, the formation of which would naturally be expected, but another acid with markedly different properties. In regard to it the authors say: "This acid is insoluble in cold water, and only slightly in hot water. It crystallizes from an alcoholic solution. It is volatile with steam. It sublimes in light flakes. The analyses did not give satisfactory results. With the small quantity at our disposal it was impossible to determine what the acid is."

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[1] This Journal, **3**, 426.

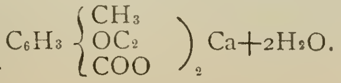
At the suggestion of Professor Remsen I have since prepared the acid in larger quantity, and have succeeded in showing what it is.

In the preparation of amido-toluic acid from the nitro-acid I found it advisable to use as little hydrochloric acid as possible, the yield being greatest under these circumstances. The preparation of the diazo-compound requires the greatest precautions. For dissolving the amido-acid very dilute nitric acid should be used. The dilute acid of the strength commonly used for a reagent is much too concentrated. It should be diluted with eight to ten times its volume of water. If this precaution is not taken, the amido-acid may easily be completely decomposed, as happened in two cases in my own experiments.

The dried diazo-compound was boiled with a considerable quantity of absolute (99 per cent.) alcohol. An abundant evolution of gas accompanied the boiling at first. After this stopped, the solution was diluted with water, when the acid under investigation was thrown down, having all the properties ascribed to it by Remsen and Kuhara. It was converted into the calcium salt, which is easily soluble in water, and crystallizes in long, white, silky needles. The analyses of the air-dried salt gave results as below:

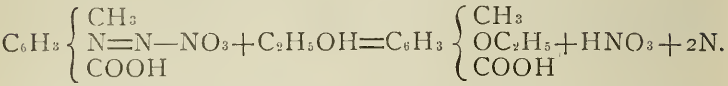
I. 0.1364 gram salt lost 0.0119 gram H_2O at 170°; and gave 0.0424 gram $CaSO_4$.

II. 0.1493 gram salt lost 0.0127 gram H_2O at 175°; and gave 0.0465 gram $CaSO_4$.

These results lead to the formula of the calcium salt of *ethoxy-metatoluic acid*,  $\left(C_6H_3\left\{\begin{array}{l}CH_3\\ OC_2\\ COO\end{array}\right.\right)_2 Ca+2H_2O.$

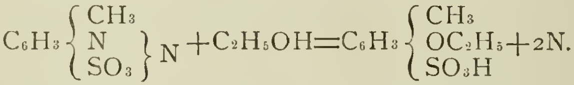
	Calculated.	Found. I.	Found. II.
Ca	10.05	10.01	10.02
H_2O	8.29	8.72	8.51

The equation representing the action described is:



$$C_6H_3\left\{\begin{matrix}CH_3\\N{=}N{-}NO_3\\COOH\end{matrix}\right.+C_2H_5OH=C_6H_3\left\{\begin{matrix}CH_3\\OC_2H_5\\COOH\end{matrix}\right.+HNO_3+2N.$$

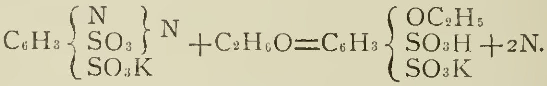
A few transformations of the same kind have already been effected. Thus Hayduck[1] obtained ethoxy-paratoluene-sulphonic acid, $C_6H_3\left\{\begin{matrix}CH_3\\OC_2H_5\\SO_3H\end{matrix}\right.$, by boiling with alcohol the diazo-compound from ortho-amido-paratoluene-sulphonic acid:



$$C_6H_3\left\{\begin{matrix}CH_3\\\left.\begin{matrix}N\\SO_3\end{matrix}\right\}N\end{matrix}\right.+C_2H_5OH=C_6H_3\left\{\begin{matrix}CH_3\\OC_2H_5\\SO_3H\end{matrix}\right.+2N.$$

Hayduck found, further, that, when methyl alcohol was used instead of ethyl alcohol, a similar reaction took place, resulting in the formation of a methoxy compound, $C_6H_3\left\{\begin{matrix}CH_3\\OCH_3\\SO_3H\end{matrix}\right.$.

Later Zander[2] obtained ethoxy-benzene-disulphonic acid, $C_6H_3\left\{\begin{matrix}OC_2H_5\\(SO_3H)_2\end{matrix}\right.$, by boiling the diazo-compound, $C_6H_3\left\{\begin{matrix}\left.\begin{matrix}N\\SO_3\end{matrix}\right\}N\\SO_3K\end{matrix}\right.$ with alcohol:



$$C_6H_3\left\{\begin{matrix}\left.\begin{matrix}N\\SO_3\end{matrix}\right\}N\\SO_3K\end{matrix}\right.+C_2H_6O=C_6H_3\left\{\begin{matrix}OC_2H_5\\SO_3H\\SO_3K\end{matrix}\right.+2N.$$

He was, however, unable to determine the relation of the groups in the compounds involved in the reaction, and hence it is at present impossible to say whether the same conditions exist in the three diazo-compounds which have yielded the peculiar results. In Hayduck's compound, as well as in that of Remsen and Kuhara, the diazo-group occupies the ortho-position relatively to methyl, and the thought first suggests itself that probably this position of the group is the immediate cause of the peculiar conduct. The question arises whether all diazo-groups which occupy the ortho-position conduct themselves in the same way.

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[1] Annalen der Chemie, **172**, 215.

[2] Annalen der Chemie, **198**, 25.

I have made some experiments with the object of answering this question, if possible. An attempt was made to study the simplest case, viz. that of orthotoluidine, but the desired transformations were not effected. Experiments with ortho-nitro-parasulphobenzoic acid also gave unsatisfactory results.

I intend, as opportunity may offer, to have further experiments made, similar to that above described by Mr. Broun. It appears probable that this anomalous conduct of diazo-compounds will be found to be connected with the position of the diazo-group.

I. R.

Johns Hopkins University, *December*, 1882.

ON COMPLEX INORGANIC ACIDS.[1]

By Wolcott Gibbs, M. D.

Rumford Professor in Harvard University.

My further investigations of the complex inorganic acids have yielded results of a very interesting character, and the field of work has become so extensive that it is simply impossible for one man to attempt to cover the whole ground. In the papers which I have already published I have described only binary compounds, such as may be expressed by the general formula—

$$mRO_3.nR'_2O_5.pR''_2O.$$

In this formula m may represent any even number from 10 to 48 inclusive, R either molybdenum or tungsten, n is 2 in the compounds described, r, p the number of molecules of base (old style), while R′ represents either phosphorus or arsenic. I have now generalized these results still further. In place of phosphorus or arsenic we may have vanadium or antimony, and probably niobium and tantalum, as I stated long since in a preliminary notice. In place of oxides of the type R'_2O_5, we may have those of the type R'_2O_3, as, for example, As_2O_3, Sb_2O_3, P_2O_3, and probably V_2O_3. Thus, the formula of a phosphoroso-molybdate of ammonium is

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[1] From a letter to the editor, dated Cambridge, Dec. 11, 1882.

$$24MoO_3.2P_2O_3.5(NH_4)_2O + 20Aq.$$

These compounds by oxidation pass into salts containing the higher oxides of the type R'_2O_5. Salts containing boric oxide, B_2O_3, have been described by Klein. Even hypo-phosphorous acid is capable of forming similar compounds. Thus, I have obtained a hypo-phospho-molybdate with the formula—

$$24MoO_3.6PO_2.6(NH_4)_2O + 7Aq.$$

Perhaps further study will show that the analyses may be represented by a simpler formula. A different mode of expression must be adopted, if, with Wurtz, we write the formula of hypophosphorous acid:

$$O = P.OH.H_2,$$

so that we have, probably, either

$$O = P.H_2.(ONH_4) \text{ or } O = P.H.NH_4.OH$$

as the term representing the phosphorus contained, the type being still $O = P \equiv (OH)_3$ as in phosphoric acid, part of the ammonium being united to WO_2 in the structural formula. Well defined and beautifully crystalline vanadio-molybdates have respectively the formulas—

$$6MoO_3.V_2O_5.2(NH_4)_2O.H_2O + 4Aq$$
$$16MoO_3.V_2O_5.5BaO.H_2O + 28Aq$$

which correspond to types of phospho-molybdates and phospho-tungstates. In like manner in two vanadio-tungstates of sodium the ratios of the tungstic and vanadic oxides are respectively as 10 : 1 and as 18 : 1.

Ternary series containing tungstic or molybdic oxide united to two other oxides also exist in large number. Thus, in the general formula—

$$mRO_3.nR'_2O_5.pR''_2O_5.rR'''_2O$$

RO_3 may be either tungstic or molybdic oxide, R'_2O_5 and R''_2O_5 two different oxides of the same type, as, for example, phosphoric and vanadic oxides. I am not prepared to say that *any* two known oxides of the type R_2O_5 may enter together into such compounds, but it is not impossible that such is the case. Examples of these salts are the following:

$$\begin{gathered} 14MoO_3.8V_2O_5.P_2O_5.8(NH_4)_2O + 50Aq \\ 48MoO_3.V_2O_5.2P_2O_5.7(NH_4)_2O + 30Aq \\ 60WO_3.V_2O_5.3P_2O_5.10(NH_4)_2O + 60Aq \\ 16WO_3.3V_2O_5.P_2O_5.5(NH_4)_2O + 37Aq \end{gathered}$$

I refrain from theory at present, and simply remark, first, that some of these compounds are almost certainly double salts, and, secondly, that in certain cases very simple formulas are obtained if we suppose that V_2O_5, with the atomic structure $V_2O_2.O_3$, may replace WO_3 or MoO_3, while with the formula V_2O_5 it replaces P_2O_5. Other ternary series contain oxides of two types united to tungstic or molybdic oxide. Thus, we have the general formulas:

$$\begin{gathered} mRO_3.nR'_2O_5.pR''_2O_3.rR'''_2O \\ mRO_3.nR''_2O_5.pR'_2O_3.rR'''_2O \\ mRO_3.nR'_2O_5.pR'_2O_3.rR'''_2O \end{gathered}$$

in which R_2O_5 may be P_2O_5, V_2O_5, As_2O_5, or Sb_2O_5, perhaps also Nb_2O_5 and Tn_2O_5, and R_2O_3 may be B_2O_3, P_2O_3, V_2O_3, As_2O_3, Sb_2O_3. You will see that such compounds may be very numerous, especially if m, n and p may vary within wide limits. There is, however, at least one other group of ternary compounds reducible to the general formula—

$$mRO_3.nR'_2O_5.pR''O_2.rR'''_2O.$$

I have obtained a few salts belonging to such series. Finally, it seems probable that there is also a series embraced in the formula—

$$mRO_3.nR'_2O_3.pR''O_2.rR'''_2O,$$

but I have not yet obtained compounds of this type.

Quaternary compounds of various types appear to exist. An example of these is the following:

$$60WO_3.3P_2O_5.V_2O_5.VO_2.18BaO + 150H_2O.$$

This is almost certainly a double or triple salt, but still shows how five different oxides may exist in a single well-defined and beautifully crystallized compound. The general formula here would be

$$mRO_3.nR'_2O_5.pR''_2O_5.qR'''O_2.rR'''_2O.$$

The possible number of combinations, if we take all the oxides not basic belonging to the four different types, and in addition give various values to m, n, p and q, must be very great.

Besides the types which I have given above I have obtained others of an entirely different character and not containing either molybdenum or tungsten. To this class belong phospho-vanadates, arsenio-vanadates and antimonio-vanadates, the general formula being

$$mR'_2O_5.nR''_2O_5.pR_2O.$$

The salts are often beautifully crystallized and well defined.

I reserve to myself the right to work in any part of this field of research, since the generalizations are exclusively my own; but at the same time I invite other chemists to enter the same field, probably the widest which has been opened up in the domain of inorganic chemistry. The results which I have given above were communicated to the National Academy of Sciences at the April and November sessions of the present year, but as some little time must elapse before I can fully complete another instalment of my work, I shall be glad if you consider this brief abstract worthy of publication in your journal.

Contributions from the Chemical Laboratory of Harvard College.

XXIX.—ON THE ACTION OF PHOSPHORUS TRICHLORIDE ON ANILINE.[1]

PRELIMINARY NOTICE.

By C. Loring Jackson and A. E. Menke.

The only paper on this subject which we have been able to find was published by M. Tait[2] in 1865. From the abstract in the Jahresbericht it appears that he obtained a semi-solid mass easily soluble in water, alcohol, and ether, which, freed from an excess of aniline, had the composition $(C_6H_5NH)_3$ P3HCl, gave a chlorplatinate, and several double salts, but yielded no satisfactory result when he attempted to set free the base. As a further investigation of Tait's substance seemed to promise interesting results, and we hoped also to obtain new compounds by varying the conditions of the reaction, we took up the study of this subject, and publish this preliminary notice in the hope of reserving it to ourselves for future work.

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[1] Presented to the American Academy, Dec. 13th, 1882.

[2] Jahresbericht '65, 411. Instit. '65, 254.

On adding phosphorus trichloride drop by drop to aniline as long as it produced a violent action, we obtained a white solid, which to our surprise was entirely different from Tait's product in that it was insoluble in ether, of a much more solid consistency, and on analysis proved to be a variable mixture of some phosphorus compound and aniline chloride, one sample containing 5.7 per cent. of phosphorus, another only 2.9, while the carbon, hydrogen, and chlorine showed as marked variations. We have not made out as yet the cause of this difference between our result and that of Tait, which is the more striking, because we took pains to follow his directions most carefully, but hope that a more complete study of the conditions of the reaction, especially in the presence of solvents, may explain the discrepancy. As the purification of this phosphorus compound offered serious difficulties, owing to its resemblance to aniline chloride in solubility, we have postponed its further study, and for the present confined our attention to one of the products of the action of heat upon it.

When the crude product of the action of phosphorus trichloride and aniline is heated over a free flame in a porcelain dish, it turns orange yellow, and gives off white fumes, which are luminous in the dark and deposit a sublimate of pure aniline chloride, as was proved by analysis. This reaction takes place slowly even at 100°, but a rapid heating at a higher temperature, as described, was found to give the best result; on the other hand the heat must not be too great, as in this case phosphoretted hydrogen is given off. The orange product boiled with alcohol gives a colorless solution and an orange residue apparently consisting of solid phosphide of hydrogen, although we have not as yet succeeded in obtaining it perfectly pure. The alcoholic solution upon addition of water throws down a white precipitate, which was purified by repeating twice the solution in alcohol and precipitation with water, and drying at 60°. The following analyses show that its formula is $(C_6H_5NH)_2POH$. It may be called therefore *dianilido-phosphorus* *hydrate*, and is probably formed by the action of the alcohol on a substance $(C_6H_5NH)_2PCl$.

I. 0.3488 gram of substance gave 0.7992 gram of CO_2 and 0.1918 gram of H_2O.

II. 0.2856 gram of substance gave 0.6502 gram of CO_2 and 0.1610 gram of H_2O.

III. 0.4623 gram of substance gave 49.9 cc. of nitrogen at a temperature of 25°, and a pressure of 766 mm.

IV. 0.3402 gram of substance gave after treatment with Na_2CO_3 and $KClO_3$ 0.1590 gram of $Mg_2P_2O_7$.

Calculated for $(C_6H_5NH)_2POH$.		Found.			
		I.	II.	III.	IV.
Carbon	62.07	62.48	62.04		
Hydrogen	5.60	6.10	6.26		
Nitrogen	12.07			12.13	
Phosphorus	13.36				13.05

The substance contains no chlorine. Analyses II, III and IV were of the same preparation. I of a different preparation.

It forms an amorphous white mass with a slight odor of phosphoretted hydrogen; melts, or rather draws together into a viscous state at 87°; is freely soluble in cold alcohol, still more so in hot, insoluble in water. It is not acted on apparently by either aqueous potassic hydrate or dilute sulphuric acid, but is decomposed by strong nitric acid.

The aqueous filtrate obtained in the purification of the foregoing substance yields on evaporation crystals, which also contain phosphorus. The investigation of the bodies mentioned in this paper, and of the many other substances, which we have reason to expect can be obtained from this reaction, will be pushed forward by us as rapidly as possible.

REVIEWS AND REPORTS.

ON SOME RECENT IMPROVEMENTS IN INDUSTRIAL CHEMICAL PROCESSES.[1]

(*Concluded from page* 311.)

The process to which I will next ask your attention is that for the manufacture of carbonate of potash, which has been invented by Professor Engel, of the Faculty of Medicine of Montpellier. Professor Engel has found that if one takes a solution of potassium chloride holding in suspension either magnesia or magnesium carbonate, and treats it by carbon dioxide, with constant agitation, one obtains a solution of magnesium chloride holding in suspension a curious double carbonate of magnesium and potassium. The composition of this double carbonate varies with the temperature employed, and with other circumstances; but, as produced by the mode of operating which Professor Engel proposes to employ industrially, the double carbonate appears to be—

$$MgKH_2CO_3,$$

or a compound of one equivalent of bicarbonate of potash with one equivalent of magnesium monocarbonate:

$$KHCO_3 + MgCO_3.$$

The existence of the double carbonate of magnesium and potassium was first made known, now many years since, by the late Henri Sainte-Claire Deville, who obtained it by the reaction on magnesium chloride of previously-formed bicarbonate of potash used in excess. Deville's method was thus the inverse of Professor Engel's, Professor Engel's double carbonate being produced by the reaction on potassium chloride of bicarbonate of magnesia in presence of magnesium monocarbonate.

As obtained by Professor Engel, the double carbonate is a crystalline powder, capable of being separated from its mother-liquor, readily and completely, by any of the ordinary methods of filtration. While quite insoluble in solution of magnesium chloride, and not at all attacked thereby in the cold, it is decomposed by pure water—slowly and only partially at ordinary temperatures, but at higher temperatures quickly and completely. Professor Engel's method of manufacturing carbonate of potash, therefore, consists in the following successive operations:

1. Injection of CO_2, preferably under a pressure of from two to three atmospheres, into a solution of potassium chloride, to which has been added the magnesium carbonate obtained in a previous fourth operation and a suitable quantity of fresh magnesia.

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[1] Read before the "Society of Chemical Industry" by Mr. Walter Weldon.

2. Separation, by means of the hydro-extractor, of the resulting double carbonate of magnesium and potassium from the solution of magnesium chloride produced at the same time.

3. Decomposition of the double carbonate, and also of the bicarbonate of potash, which is one of its constituents, by boiling the double carbonate with water. (This operation is performed in closed vessels, in order that the CO_2 evolved during the reduction of the bicarbonate of potash to the state of normal carbonate may be collected for use again.)

4. Separation, by means of the hydro-extractor, of the solution of potassium carbonate obtained in the third operation from the magnesium carbonate, which it at first holds in suspension.

5. Evaporation of the filtrate from the fourth operation to dryness.

The magnesium carbonate separated in the fourth operation goes back into the next first operation. To it has to be added each time a quantity of fresh magnesia equivalent to the magnesium chloride produced in the first operation. The fresh magnesia is obtained by heating magnesite in a current of steam. Carbon dioxide is of course obtained at the same time, and the CO_2 from this source, together with that driven off from the double carbonate in the fourth operation, make up, if all loss be avoided, the total quantity of CO_2 required.

Many years ago, when I was as yet without any practical chemical experience, and was foolish enough to think that a merely literary acquaintance with chemistry was sufficient to enable one to invent new industrial chemical processes, I secured a patent for treating sodium chloride exactly as Professor Engel treats potassium chloride. I expected that by so doing I should obtain magnesium chloride and bicarbonate of soda. Subsequent experience showed that while sodium chloride can be decomposed by bicarbonate of magnesia, if sufficient pressure be used, the amount of pressure required is far too great to permit of the reaction being performed industrially; and to this fact is due a merit of Professor Engel's process which is of very great practical moment. We know that, for many of the purposes for which carbonate of potash and caustic potash are used in the arts, the presence with them of even only minute quantities of soda is very prejudicial; and we also know that nearly all commercial potassium chloride has associated with it appreciable proportions of sodium chloride. From a mixed solution of potassium and sodium chlorides, however, Professor Engel's process will precipitate the whole of the potassium as double carbonate, the whole of the sodium chloride remaining in solution, absolutely unchanged. On the sole condition that the double carbonate produced by his first operation be washed completely free from mother-liquor, as it readily may be, his final product must, indeed, be almost chemically pure. It cannot contain any foreign bodies whatever, except such as it may take up from the material of the vessels in which the filtrate from the fourth operation is evaporated down.

Though the Engel process is not yet in industrial operation, active steps are being taken to the end that it soon shall be. The process was tested on a semi-industrial scale at Montpellier last spring, and the results obtained led to the formation of a "Société de Carbonate de Potasse"—to which I have been invited to become Ingénieur Conseil—and this Société began some months ago to build a factory at Havre, and has just bought land for a second factory at Stassfurt. The factory at Havre is expected to be at work before the end of this year.

Another French process for the manufacture of carbonate of potash is further advanced. I refer to the trimethylamine process, which the Société de St. Croix, whose works are situated near Lille, is now practising on a somewhat considerable scale. We all know that the "ammonia process," now so largely used for the manufacture of soda, cannot be used for the manufacture of potash, by reason of hydro-potassic carbonate being too soluble in solution of ammonium chloride. Bicarbonate of potash, however, is but very slightly soluble in solution of chloride of trimethylamine; and trimethylamine, thanks to the admirable invention of my friend, Professor Camille Vincent, of the École Centrale, is now placed, as the French say, at the door of all the world. Though so rare a substance a very short time ago, it is now cheaper, I believe, equivalent for equivalent, than ordinary ammonia. I am not acquainted with the details of the process by which the Société de St. Croix manufactures potash by means of this compound ammonia. I am not acquainted with any of the members of that Société, and I am told that they wish to keep the details of their process secret. An account of the theory of the process, however, was recently published by its inventors, MM. Ortlieb and Müller, in the *Bulletin Scientifique du Départment du Nord;* and as that journal probably does not circulate largely among the members of this Society, and as I have not seen the memoir of MM. Ortlieb and Müller copied into any other journal, I may perhaps be allowed to briefly indicate the chief point which it brings out. The chemistry of the trimethylamine potash process appears to differ from that of the ammonia soda process otherwise than merely in the nature of the ammonia employed. The first step in the ammonia-soda process is to form ammonia bicarbonate; but no bicarbonate of trimethylamine is known to exist. The highest carbonate of trimethylamine which can be obtained in the free state, under any conditions at present known, is the sesquicarbonate; and the reaction of sesquicarbonate of trimethylamine upon potassium chloride, if indeed, strictly speaking, any such reaction can be said to take place at all, is more complex than the reaction upon sodium chloride of bicarbonate of ordinary ammonia. In the latter case we have an ordinary double decomposition, followed or accompanied by a not very large amount of inverse reaction. We may say that all the ammonium bicarbonate undergoes conversion into ammonium chloride, and that all the sodium chloride undergoes conversion into bicarbonate of soda, but that the whole of the bicarbonate of soda formed does not precipitate, owing to this salt being as soluble in solution of ammonium chloride as in pure water, and that between a part of that portion of it which dissolves in the mother-liquor and some of the ammonium chloride of the mother-liquor, reverse reaction takes place. Still, the essential reaction of the ammonia-soda process is of the nature of a simple interchange of constituents between two salts, reacting upon each other, equivalent for equivalent. With sesquicarbonate of trimethylamine and potassium chloride, however, the case is otherwise. One has to use several equivalents of sesquicarbonate of trimethylamine per equivalent of potassium chloride, and one obtains, mixed with sesquicarbonate of trimethylamine, which has undergone no change, one equivalent of bicarbonate of potash, one equivalent of chloride of trimethylamine, and one equivalent of what MM. Ortlieb and Müller call sub-sesquicarbonate of trimethylamine, being a body containing four of trimethylamine and five of carbonic acid. MM. Ortlieb and Müller explain what takes place by supposing that sesquicarbonate of trimethylamine is really a compound of sub-sesquicarbonate with an unstable bicarbonate, incapable of existing by itself; and that in their process a portion of the sesquicarbonate splits up into these two constituents, of which the latter only then reacts upon the potassium chloride. Be that as it may, it would seem that to decompose one equivalent of potassium chloride MM. Ortlieb and Müller require to use six equivalents of trimethylamine and nine equivalents of carbonic acid. And yet it is certain that their process is so far a commercial success that the German manufacturers of potash by the Leblanc process are already feeling the competition of the Société de St. Croix very keenly.

I may just add that the trimethylamine process is available for the manufacture of potash only from potassium chloride. Upon potassium sulphate, sesquicarbonate of trimethylamine has no action. Hence the Société de St. Croix cannot use the potash salts—15 or 16 per cent. of which are sulphate—of which some four or five thousand tons a year are produced in their own Department of France from the residue of the distillation of alcohol from the product of the fermentation of the molasses produced in beet-root sugar factories; but they have to fetch their potassium chloride all the way from Stassfurt. The fact that they can, nevertheless, compete with the German makers by the old process is of course all the more remarkable.

The Engel process is not thus limited as regards its raw material. It can transform potassium sulphate into carbonate as readily as potassium chloride.

Some expectation has been entertained that trimethylamine might be used instead of ordinary ammonia in the ammonia-soda process;

and MM. Ortlieb and Müller show that sesquicarbonate of trimethylamine reacts upon both sodium sulphate and sodium chloride in the same manner as upon potassium chloride. To substitute, however, six equivalents of a body having a high molecular weight for one and a half to two equivalents of a body having a much lower molecular weight, would be hardly rational; and we may therefore take it that the industrial applications of trimethylamine will be confined to purposes to which ordinary ammonia is not applicable.

I can hardly pass from the trimethylamine potash process without expressing my curiosity as to how the Société de St. Croix has got over the difficulty which one would have thought there must have been to get workmen to manipulate trimethylamine. I have not worked with trimethylamine myself, and I am acquainted with its peculiar odor only by reputation. From all I am told, however, that acquaintance with it is quite close enough. Friends in France have more than once offered me a few litres of trimethylamine for my laboratory, but always with a strong recommendation that I should not accept them. They assure me that the odor of very putrid herring is almost pleasant in comparison with that of commercial trimethylamine, and that the latter is not only so powerful and offensive but also so clinging and persistent that to merely pour a little trimethylamine from a bottle into a beaker is to condemn yourself to seclusion from all decent society for a somewhat considerable time. How the Société de St. Croix manages in this matter I should like to know.

I have only one other new French process to touch upon, and that is the process of MM. Benker and Lasne for economizing nitrous compounds in the manufacture of sulphuric acid. Some of the members present are perhaps only too well aware that the whole of the nitrous compounds contained in the gases from the vitriol-chambers does not undergo absorption in the Gay-Lussac tower, and MM. Benker and Lasne believe that they have proved that one reason of this is that NO_2, at any rate under the conditions which obtain in the Gay-Lussac tower, does not form with sulphuric acid any stable compound. A portion, at any rate, of the nitrous compounds in the exit-gases from the vitriol-chambers is unquestionably there as NO_2, and some authorities are of opinion that NO_2 can, and does in the Gay-Lussac tower, react on sulphuric acid, forming nitrosulphonic acid and nitric acid, both of which are then retained in solution by the excess of sulphuric acid, which is of course always present. MM. Benker and Lasne hold, on the contrary, that the only oxide of nitrogen which can form a stable compound with sulphuric acid is nitrous anhydride, or N_2O_3; and, therefore, that for the NO_2 in the chamber-gases to be absorbed in the Gay-Lussac tower, it must be reduced to N_2O_3 before it reaches the Gay-Lussac tower. In order thus to reduce the NO_2 in the chamber-gases before these reach the Gay-Lussac tower, MM. Benker and Lasne inject into the conduit conveying the exit-gases from the last chamber to the foot of the Gay-Lussac tower a regulated quantity of SO_2, accompanied by just the quantity of vapor of water necessary to form, with the $SO_2 + NO_2$, nitrosulphonic acid. There can be no doubt that in one or two French works this expedient has reduced the consumption of nitre, per given quantity of sulphuric acid produced, to less than one-half the lowest proportion to which it had ever previously been reduced in any sulphuric acid work whatever; but in some other French works, and in several English works into which I have been the means of introducing MM. Benker and Lasne's process, it has not as yet given equally satisfactory results. This can only be due to some difference between the mode in which the chambers are conducted in the works in which the process gives good results, and the mode in which the chambers are conducted in the works in which it has as yet been less successful; but what the nature of that difference is has for some months past puzzled us greatly. MM. Benker and Lasne, however, now believe that they have at last solved the difficulty; and I am going to Paris to-morrow to learn how.

A plan of another kind for accomplishing the same object has just been patented by the Compagnie de St. Gobain. I have no details of its results, though I hope to visit Chauny and obtain such this week. It consists in making the gases which have traversed the ordinary Gay-Lussac tower afterwards traverse several supplementary towers, supplied with weaker sulphuric acid than is supplied to the Gay-Lussac tower itself. I am informed that the acid running from the supplementary towers is found to contain dissolved in it appreciable quantities of nitric acid.

From the "pleasant land of France" I will now ask you to pass for a few moments to a spot on the banks of the Elbe, situated at the northern extremity of the district known as "Saxon Switzerland," the interest of which district, due to its wonderful picturesqueness, and to the association of so many points of it with song and legend, is heightened to some minds, including my own, by the fact that the rocks by which its mountains are chiefly composed contain not less than 11 per cent. of potash and 4 per cent. of lithia. I refer, of course, to Aussig, in Bohemia. At the splendid works of Dr. Max Schaffner, at Aussig, my friend and fellow-member, Mr. J. C. Gamble, and myself saw in operation, on an experimental scale, three years ago, a process for recovering sulphur from alkali-waste, which, with some modifications, is now likely to prove of very exceptional importance. This method, the joint invention of Dr. Schaffner and Mr. W. Helbig, the manager of the Aussig works, differs from all other processes for the same object which have attained any measure of practical success in three very important particulars. All other processes consume hydrochloric acid, recover only a portion of the sulphur contained in the waste treated, and recover none of the calcium contained in it; but Messrs. Schaffner and Helbig's process requires no acid, recovers the whole of the sulphur originally contained in the waste, and, in addition, recovers all its calcium as carbonate. As originally devised and as Mr. Gamble and I saw it in operation on the occasion in question, it included three operations, the first of which consisted in heating fresh waste with solution of magnesium chloride, in a closed iron vessel furnished with a mechanical agitator. Under such circumstances two successive, though practically simultaneous double decompositions take place. Calcium sulphide and magnesium chloride decompose each other, producing calcium chloride and magnesium sulphide, and then this last reacts upon some of the water present to produce magnesia and sulphuretted hydrogen. The sulphuretted hydrogen is evolved in a continuous stream until the charge of waste is completely decomposed, and there then remains in the boiler a solution of calcium chloride holding in suspension an equivalent of magnesia. MM. Schaffner and Helbig pointed out to us that as the sulphuretted hydrogen obtained in this way cannot but be absolutely pure, its application to the production of SO_2 for use in vitriol-chambers would be free from all the inconveniences experienced when attempting to manufacture sulphuric acid from such mixtures of sulphuretted hydrogen and carbon dioxide as are obtained by treating the ammoniacal liquors of gas-works by an acid; but they then preferred to treat their sulphuretted hydrogen for the obtainment of free sulphur from it. They had discovered a very simple means of realizing the theoretical reaction:

$$2H_2+SO_2=2H_2O+3S.$$

All others who had tried treating together H_2S and SO_2 had found that the product consisted largely of pentathionic acid; but MM. Schaffner and Helbig had found that if the two gases be caused to react upon each other in presence of not less than a certain quantity of solution of either calcium chloride or magnesium chloride, either no pentathionic acid is formed at all, or, if any be formed, it is immediately decomposed, with a result that all the sulphur of both gases is obtained in the free state. The second operation which Mr. Gamble and I saw at Aussig was accordingly conducted as follows: First, one-third of the sulphuretted hydrogen was burnt into SO_2 and steam. (Some two hundredweight or so of sulphur were being produced per day, but the operation of burning one-third of the H_2S corresponding to that quantity of sulphur consisted simply in permitting the H_2S to issue from a couple of fish-tail burners, and then setting light to it, when the jets of H_2S went on burning as regularly and placidly as jets of coal-gas could have done.) Secondly, the products of the combustion of one-third of the H_2S were mixed with the other two-thirds of it, and the resulting mixture was then sent in at the bottom of a small tower, packed pigeon-hole fashion, with blocks of wood, down which was kept trickling solution of calcium chloride. There continually issued from the bottom of the tower a thin magma, consisting of solution of calcium chloride holding in suspension free sulphur. After the separation of the sulphur by filtration the solution of calcium chloride was used again indefinitely.

By these two operations, then, practically the whole of the sulphur of the waste treated was obtained in the free state. The remaining operation consisted in injecting CO_2 into the solution of calcium chloride holding magnesia in suspension which had been obtained as the residual product of the first operation, thereby reproducing the quantity of magnesium chloride which had been commenced with, and at the same time regenerating all the calcium carbonate which had been employed for the production of the black ash of which the waste had been one of the constituents. The net result of the three operations thus was that from the waste treated were obtained practically all its sulphur in the free state, and practically all its calcium as carbonate, without consumption of anything but coal and labor.

What appeared to me the weak point in this very remarkable process lay in its third operation. I had had some experience of the reaction upon which that third operation is based some eleven or twelve years before, when I had endeavored by the same reaction to transform into magnesium chloride the calcium chloride obtained by decomposing manganese chloride by lime; and I am afraid that to the impression then made upon my mind by the comparative slowness of the reaction in question is at least partially due the fact that nothing was done in this country with MM. Schaffner and Helbig's process until a few months ago, when it was taken in hand by one of our Vice-Presidents, Mr. Alexander Chance, of Birmingham, who has since been experimenting upon it with a degree of spirit and liberality which I cannot enough admire. Before I had seen the process in experimental operation at Aussig, Dr. Schaffner had asked me, and I had agreed, to undertake its exploitation in this country; and after having seen it, I brought it under the notice of nearly all those English manufacturers of alkali who make chlorine as well; but as I could not tell them either that Dr. Schaffner was himself performing the process on an industrial scale, or that I could regard the industrial practicability of its third operation as being as yet absolutely established, none of them cared to do more than discuss the matter. Mr. Chance does not make chlorine—I have rarely occasion to meet alkali manufacturers who are not also chlorine manufacturers—and Mr. Chance first learnt of the process from Dr. Lunge's book. He immediately began to experiment with it on a scale, not of hundredweights, but of tons of waste per operation, and he soon came to see that if the whole of the H_2S evolved in its first operation were burned, and the resulting SO_2 sent into the vitriol-chambers, the cost of the process would be practically simply the cost of the operation of regenerating the magnesium chloride. To convey the waste from the vats to the "stills" in which it is to be treated by magnesium chloride is certainly no more costly, and in many cases would be much less costly, than the methods of disposing of it which are at present in use; and the temperature to which it suffices to raise the contents of the still is so low, and the reaction which goes on in them takes place so readily, that the cost of the operation for steam and superintendence must be more than counterbalanced by the less cost for labor and plant of obtaining SO_2 by combustion of H_2S than the cost for the same items of obtaining SO_2 by the combustion of the sulphur in pyrites. The manufacturer can therefore afford a certain amount of pumping for the regeneration of his magnesium chloride, apart from the consideration that the calcium carbonate regenerated at the same time will at least pay a part, if not the whole, of the cost of it. It is to this point of the regeneration of the magnesium chloride that Mr. Chance has recently devoted his chief attention. Mr. Chance is with us this evening, and I believe he is prepared to tell you that he regards the industrial practicability of the reaction

$$CaCl_2 + MgO + CO_2 = MgCl_2 + CaCO_3$$

as being now *un fait accompli.*

While, however, Mr. Chance has thus been devoting a very rare amount of skill and enterprise and enthusiasm to the industrial realization of the third operation of the original form of MM. Schaffner and Helbig's process, those gentlemen themselves have been endeavoring to so modify their process that that third operation shall, at least in certain cases, be no longer necessary. I am extremely sorry that I have not as yet permission to make the new form of their process public. I hope to have the privilege of bringing it before you on some future occasion; but all that I can say of it now is that it provides for the regeneration of the magnesium chloride by a method which involves no pumping at all, and which is entirely paid for by subsidiary advantages. The new method is not one which will be absolutely universally available. The original method will still have to be resorted to in some cases. But between the two methods I feel the utmost confidence that the good old Leblanc process—for, although somewhat of a Radical in politics, and somewhat of a *révolutionnaire* in relation to the chemical industries, I am almost a Tory in respect of what has certainly been hitherto the most important and beneficent industrial chemical process ever invented—I feel, I say, completely convinced that the Leblanc process, instead of being superseded by the ammonia process, will at least be able to hold its own side by side with the ammonia process; that it will be possible by-and-by to render the Leblanc process as inoffensive as the ammonia process; and that, eventually, manufacturers using the Leblanc process will not only cease to accumulate waste-heaps, but become as independent of pyrites-mines as manufacturers of chlorine are of mines of manganese.

The process of MM. Schaffner and Helbig, however, is available only for the alkali-waste of the future—that is to say, it is available neither for old waste nor for the yellow liquors given off by old waste-heaps. The present waste-heaps, for years after all addition to them shall have ceased, will continue to give off yellow liquors; and wherever these liquors can be collected it will be necessary to collect them, and to treat them for the recovery of sulphur from them. It has seemed to me that there are one or two localities in which one could treat these liquors very economically by a method, which, unlike those practised by Mr. Mactear at St. Rollox, and M. Pechiney at Salindres, would not require any hydrochloric acid. Instead of hydrochloric acid one might use, it seems to me, the solution of iron chloride, which is a residue of the wet process of extracting copper from burnt pyrites. There are watercourses within my knowledge which are continually receiving both the drainage from waste-heaps and copper-extractors' residual liquor. One of the results is, of course, a horrible pollution of the neighboring atmosphere by sulphuretted hydrogen, this sulphuretted hydrogen being, at least mainly, due to the reaction—

$$CaSH_2S + FeCl_2 = CaCl_2 + FeS + H_2S.$$

The other reaction which takes place when the drainage from waste-heaps comes into contact with ferrous chloride may be represented by the equation—

$$CaS_2 + FeCl_2 = CaCl_2 + FeS + S$$

so that the total products of the reaction of ferrous chloride on yellow-liquor are calcium chloride, ferrous sulphide, free sulphur, and sulphuretted hydrogen. If, however, there were present with the ferrous chloride a sufficient quantity of any oxide of iron, the sulphuretted hydrogen would be decomposed as it was formed, and the final result would be simply a mixture of ferrous sulphide and free sulphur suspended in solution of calcium chloride. The mixture of ferrous sulphide and free sulphur would at first be bulky, but if it were simply left in heaps for a time—say, on the top of the waste-heaps themselves—it would diminish in bulk, and its ferrous sulphide would, for the most part, become oxidized into Fe_2O_3 and free sulphur. The sulphur of the mixture could then be readily burned off, if not in ordinary pyrites-burners, certainly in the so-called "shelf-burners" which are so generally used on the Continent, and are now coming into extensive use in this country. To turn to account in this way, however, the ferrous chloride of copper-extractors' residual liquors, it would be necessary first to free those liquors from the sodium sulphate they contain, as otherwise the mixture of ferrous sulphide and free sulphur would be mixed with more than its own weight of calcium sulphate. For this purpose I would propose to employ a third residual product—namely, the solution of calcium chloride, which is the only residual product of the manufacture of chlorine. The operations to be performed would thus be two. First, copper-extractors' residual liquor and solution of calcium chloride should be pumped simultaneously into a large wooden vessel furnished with a mechanical agitator, and then, when the right proportion of each liquor has been pumped in, the contents of the vessels should be run on to a filter-bed, from which the filtrate should flow to a second wooden vessel furnished also with a mechanical agitator. In this second vessel there should be added to the filtrate either the quantity of lime necessary to decompose a part of the ferrous chloride, so as to produce a quantity of ferrous protoxide equivalent to the quantity of H_2S which would otherwise be evolved in the second operation, or preferably, a quantity of finely-divided Fe_2O_3 residue of the operation of burning of the sulphur from a previously-formed quantity of final product. The second operation would then consist simply in pumping into this second vessel yellow-liquor as long as it continued to be decomposed. I think that this manner of proceeding would be effective; it certainly would not be costly; and for two very offensive solutions which now pollute the streams, and also, by one of the products of their reaction on each other, the atmosphere of certain districts, it would substitute an innocuous solution of calcium and sodium chlorides.

In conclusion, I would beg to touch for a moment on a recent improvement in the manufacture of chlorine. In the process by which nearly the whole of the chlorine made in the world is now manufactured, aqueous hydrochloric acid is treated by a "mud" consisting of a compound of artificial manganese dioxide with lime and other protoxides suspended in solution of calcium chloride. If the hydrochloric acid employed were pure, the only products of this treatment would be free chlorine and a residual mixed solution of manganese and calcium chlorides: but as the hydrochloric acid used always contains sulphuric acid, calcium sulphate is formed also; and before the solution can be treated for the reconversion of its manganese into a state in which it can again liberate chlorine from HCl, this calcium sulphate has to be got rid of. To this end, the solution is allowed to repose until the calcium sulphate is deposited; the clear part of the solution is then decanted, and the residual mixture of calcium sulphate and mother-liquor is then passed through the filter-press. These operations all involve a certain amount of cost. While the calcium sulphate is being allowed to settle, the solution cools, and the heat which it thus loses has afterwards to be restored to it; the treatment of the deposit by the filter-press costs at least something for labor and steam; and though the filter-press separates from the magma of calcium sulphate and mother-liquor the greater portion of the latter, it does not separate the whole, and there is therefore lost with the calcium sulphate a certain proportion of manganese chloride. These inconveniences have led to many attempts to purify from sulphuric acid the hydrochloric acid used in the manufacture of chlorine before admitting it into the chlorine stills; but no such attempt had practically succeeded until about a year ago, when Mr. W. G. Strype, C. E., of the Dublin and Wicklow Manure

Company's works, at Wicklow, realized a method of purifying hydrochloric acid from sulphuric acid by means of calcium chloride. While calcium sulphate is somewhat freely soluble in hot hydrochloric acid, it is only slightly soluble in cold hydrochloric acid; and what Mr. Strype therefore does is to add to his hydrochloric acid, in the cold, about 20 per cent. of its volume of the solution of calcium chloride, which is obtained as a by-product of the regeneration of his manganese, and which, therefore, costs him nothing. He finds that he can thus precipitate as calcium sulphate, very nearly, though not quite, the whole of the sulphuric acid originally present in his hydrochloric acid; and a very simple filter, which he has devised for the purpose, enables him to separate his purified hydrochloric acid from the calcium sulphate so formed at a barely appreciable expense.

When Mr. Strype informed me of the results of his preliminary experiments on this matter, I at once saw that they opened the way to the realization of a method of working in the manufacture of chlorine which would effect a very important economy, additional to those already indicated. Even artificial, finely-divided, hydrated manganese dioxide will not react upon aqueous hydrochloric acid of more than a certain degree of dilution. Hence, when one adds gradually to hot aqueous hydrochloric acid that "manganese mud" of which I spoke, there comes a moment when the mud will no longer dissolve integrally. The acid in the "stills" in which the operation is performed has become so dilute that the only constituents of the mud which it can now react upon are the protoxides in it. If, after this point has been reached, one went on adding mud, the protoxides in the further quantity of mud added would completely neutralize the remainder of the acid, but the MnO_2 of this further quantity of mud would remain undissolved. When working with hydrochloric acid containing sulphuric acid, one cannot thus add mud after it ceases to dissolve completely, because, if one did, one would obtain a residual solution holding in suspension not only MnO_2, but also $CaSO_4$; and one could not remove the $CaSO_4$ from this solution without also removing, and losing, the MnO_2. The custom has therefore been, and still is, everywhere except in Mr. Strype's works, to cease sending mud into the chlorine stills when the moment has arrived at which, if more mud were added, the MnO_2 in it would not dissolve; and when that moment has arrived the contents of the stills are run off into "wells," in which they are then agitated, for the neutralization of the free acid remaining in them, with finely-divided limestone. The acid which is so neutralized by limestone is, of course, lost; the limestone employed to neutralize it is also lost; and the operation of neutralization requires an appreciable amount of steam and labor. I suggested to Mr. Strype that his purified acid would enable him to avoid both this loss of acid and this consumption of limestone; and I am glad to be able to say that the suggestion has been realized. During nearly the whole of last year Mr. Strype has worked, and he is still working, as follows: Using in his stills hydrochloric acid from which he has first separated the greater portion of the sulphuric acid originally contained in it, he conducts his stills in the ordinary way, running off from them acid "still-liquors" into the ordinary neutralizing wells, but there treating the acid liquors—not absolutely every time, but by far the greater number of times—instead of with limestone dust with manganese mud. The neutralization of the acid liquors by manganese mud occupies only a few minutes; and when the neutralized liquors reach the settlers, the MnO_2 in suspension in them settles so rapidly as to permit settled liquor to reach the oxidizers at such a temperature as not afterwards to require the usual "heating-up" by injection of steam. The MnO_2 which deposits in the settlers is from time to time added to the ordinary mud used in the stills. As Mr. Strype's purified hydrochloric acid, however, still contains a little sulphuric acid, and as calcium sulphate accordingly gradually accumulates in his mud, from time to time he has to intercalate an operation of neutralization by the old way; but this happens only so rarely as to still leave it practically the case that the method of working which he has adopted, besides economizing apparatus, steam and labor, and reducing the loss of manganese to considerably below one per cent., also economizes all the limestone used by others for the neutralization of their still-liquors, and at the same time the quantity of acid equivalent to that quantity of limestone. Mr. Strype thus obtains seven tons of bleaching powder from the quantity of acid from which no one else at present gets more than six tons, and from which very few manufacturers get so much as six tons, while, moreover, realizing appreciable economies at all other points.

PHYSIOLOGICAL OXIDATION.

One of the first attempts to explain, by experimental methods, the oxidation processes which take place in animal bodies was made by Schmidt[1] in 1862. Finding that the red corpuscles have the power of giving a deep blue color with guaiac tincture, he concluded that ozone was present in the blood. Schönbein[2] was also of the opinion that physiological oxidation is brought about by ozone in the blood, but subsequent investigations by Huizinga,[3] and more recently those of Nasse,[4] have shown that, not only is ozone absent in animal bodies, but that oxidation is due to atomic or active oxygen. Hoppe-Seyler and his pupils have found that oxygen combined with hæmaglobin does not effect oxidations, and that oxyhæmaglobin is very probably a compound consisting of a molecule of hæmaglobin united to a molecule of oxygen ($Hb+O_2$). It has also been shown that very little oxidation takes place in the blood, but that it takes place mainly in the tissues themselves. These facts lead us to conceive of the process of physiological oxidation as being carried on somewhat in the following way: The atmospheric oxygen is taken up by the blood in the lungs, and, uniting with the hæmaglobin, it forms a compound which of itself has no oxidizing power. In the capillaries this oxyhæmaglobin is dissociated, the oxygen O_2 passes through the walls of the capillaries into the surrounding tissues, and there in some way is made active, *i. e.* is decomposed into its atoms, and these unite with the oxidizable constituents of the tissues.

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[1] On ozone in the blood. Dorpat, 1862.
[2] Sitzungsber. d. bayr. Acad. d. Wiss. zu München **1**, 274.
[3] Virchow's Archiv, **42**, 359.
[4] Pflüger's Archiv, **3**, 205.

Various hypotheses have been suggested to account for the active condition of oxygen in the tissues; prominent among these is that of Hoppe-Seyler.[1]

In studying the processes of putrefaction he observed that free hydrogen is given off in those cases in which oxygen is not present, and that whenever oxygen has access to decaying liquids, not only is all the hydrogen oxidized, but energetic oxidation processes are observed as well. The simplest explanation of this seemed to be that the nascent hydrogen has the power of splitting up the oxygen molecule, uniting with one atom and setting the other free; and to the free atoms thus formed are to be attributed the strong oxidations which take place in decaying bodies. To test this hypothesis he made experiments with palladium hydrogen. The energetic reducing powers of this compound were described by Graham; that it can also cause oxidation, Hoppe-Seyler showed by bringing some strips of palladium foil charged with hydrogen into a solution of indigo in the presence of air. The solution soon became yellow, and after a time the indigo was completely destroyed. If palladium hydrogen be brought into a neutral solution of potassium iodide and starch, the liquid becomes blue in a few minutes, after which the starch is slowly destroyed. In a similar way benzene was oxidized to phenol; so, too, petroleum ether when brought in contact with sodium and exposed to the air takes up oxygen and forms small quantities of volatile acids. "These experiments and others of a similar nature," he asserts, "admit of no explanation other than that the active hydrogen renders the oxygen active, and, since the former unites with oxygen, we cannot well conceive of the process without supposing that the hydrogen in uniting with one atom of the molecule O_2 sets the remaining atom free, thus making it active." "Just as the hydrogen atom cannot exist in a free state, so the active oxygen, if no oxidizable material is present, unites with water to form hydrogen dioxide, or with inactive oxygen to form ozone."

In common with Claud Bernard and E. Mitscherlich, Hoppe-Seyler compares the life of organisms to a process of decay, and states that, although our knowledge of the processes which take place in the organs of plants and animals is so fragmentary that but few trustworthy facts are known upon which to base the comparison, still he regards it as neither premature nor superfluous to carry it out as far as possible, because there are no facts known which disprove it, and because it affords starting points for future investigations. Just as decaying substances give off nascent hydrogen which, in the presence of oxygen, can make the latter active, so in animal tissues he is inclined to assume that the oxygen is rendered active by the same means.

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[1] Zeitsch. phys. Chem. **2**, 22. Berichte d. deutsch. chem. Gesells. **12**, 1551.

Closely related to this hypothesis are the recent investigations of Moritz Traube on the active condition of oxygen. His first paper, in which he considers the formation of hydrogen dioxide by oxidation processes, was reviewed in an earlier number of this journal, Vol. 4, p. 73. In a second communication[1] on the theory of the formation of active oxygen by means of nascent hydrogen and palladium hydrogen, he considers Hoppe-Seyler's hypothesis in detail. In regard to the occurrence of hydrogen in animal bodies he says: "Hitherto this gas has only been detected in the alimentary canal, where, as is well known, processes of decay are brought about by bacteria. If putrefaction and life are similar from a chemical standpoint, then in animal bodies soon after death when respiration has ceased, hydrogen should be evolved, for decaying animal matter in the absence of oxygen is known to give off hydrogen. This is by no means the case. An accumulation of gas-bubbles in the blood, or a swelling of the tissues of an animal which has been dead but a short time, has never been noticed. On the contrary, blood and muscles may be preserved at ordinary temperatures for days without becoming charged with gases."

"The researches of van den Broeck[2] have shown that fresh blood, albumen, etc., may be preserved for several weeks, when bacteria are excluded, without a trace of gas being formed. There is, therefore, no observation known which even suggests the formation of hydrogen in the animal body."

He now describes some experiments which were undertaken to show that there is a distinct difference between putrefaction brought about by bacteria and the vital processes of animals. A piece of decaying meat treated with a solution of potassium nitrate was allowed to stand five hours. On testing the solution with iodide of zinc and starch a distinct reaction for nitrous acid was obtained. A piece of fresh muscle treated in the same way gave the reaction for nitrous acid only after standing for three days, when decomposition had begun. Nascent hydrogen cannot therefore be present in muscles, for in a short time the nitre would have been reduced, not to nitrous acid, but to ammonia.

A second characteristic property of bacteria is their power of transforming nitrogenous nourishment into ammonia compounds.

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[1] Berichte d. deutsch. chem. Gesell. **15**, 2421.

[2] Annalen der Chemie, **115**, 78.

Decaying liquids always become ammoniacal, but animal bodies contain only traces of ammonia compounds, and in the normal state neither the tissues nor the secretions and excretions give an ammoniacal reaction. Traube therefore concludes that the transformation of matter in animals is evidently different from that in bacteria ; and, as it has been shown that hydrogen is not formed in the tissues, we cannot suppose that the formation of active oxygen in animal bodies is due to nascent hydrogen.

He now considers the chemical part of the hypothesis, viz. that nascent hydrogen can render oxygen active. Hoppe-Seyler's experiment with petroleum ether and sodium he shows to be unreliable, and calls attention to the fact that Fudakowski[1] has shown that petroleum benzine has the power of taking up oxygen at ordinary temperatures without the presence of sodium. He then made the following experiments : Nascent hydrogen was prepared by the action of dilute sulphuric acid on zinc ; that the hydrogen at the moment of its liberation is exceedingly active, and has reducing powers which are not possessed by the molecules of hydrogen gas at ordinary temperatures, is well known. Now this nascent hydrogen, when brought in contact with oxygen, if Hoppe-Seyler's hypothesis is correct, should give active oxygen or ozone. But not a trace was formed. And thinking that an objection might be raised by supposing the ozone to be destroyed by the zinc, he added indigo sulphuric acid (which can be easily oxidized) to the sulphuric acid. On adding strips of zinc to the solution, and shaking for twenty minutes, the blue color was not destroyed, showing that neither active oxygen nor ozone was formed. Nascent hydrogen made by the action of zinc on caustic soda was shaken with air and ammonia ; if active oxygen had been formed, some of the ammonia would have been oxidized to nitrous or nitric acid, but the experiment showed that not a trace of either was formed. Traube, therefore, regards it as proved that nascent hydrogen has not the power of forming active oxygen, and further shows that nascent hydrogen cannot form hydrogen dioxide with oxygen in the presence of water, because the hydrogen reduces the dioxide, forming water.

These experiments led him to suspect that the oxidations observed by Hoppe-Seyler with palladium hydrogen were not brought about by nascent hydrogen. A simple experiment with palladium hydrogen showed that it too, like zinc and other substances which oxidize in the presence of air and water, has the power of forming hydrogen dioxide. In previous experiments he had shown that when zinc is oxidized under these conditions, no ozone or active oxygen is formed, but simply hydrogen dioxide, and it seemed probable that the oxidations were due to the compound. But Hoppe-Seyler had shown that potassium iodide and starch solution in the presence of air and palladium hydrogen are colored blue, and it is known that dilute hydrogen dioxide alone cannot effect this. He therefore suspected that the metallic palladium played a part in the reaction, and in some way acted as a carrier of oxygen from the hydrogen dioxide to the potassium iodide. The correctness of this supposition was shown as follows: After shaking palladium hydrogen for ten minutes with air and a solution of potassium iodide and starch, the solution was still colorless: that hydrogen dioxide was present was shown by adding a drop of ferrous sulphate to a portion of the colorless solution, when a heavy blue precipitate was formed. The remainder of the solution was decanted from the palladium hydrogen and poured into three flasks. To the solution in the first flask a piece of palladium foil (ignited and free from hydrogen) was added, to the second a piece of palladium hydrogen. The flasks were then completely filled and corked to exclude air. A blue color was formed only in the first flask, thus showing that metallic palladium, like platinum and ferrous sulphate, has the power of transferring oxygen from hydrogen dioxide to potassium iodide and causing the liberation of iodine. The second flask showed that palladium hydrogen has not this power, and the third flask, to which nothing had been added, showed that a dilute solution of hydrogen dioxide does not give a blue color with potassium iodide. The same results were obtained by repeating the experiment and using a solution of hydrogen dioxide prepared from barium dioxide. Hence the oxidation of potassium iodide with palladium hydrogen, observed by Hoppe-Seyler, is not due to active oxygen, but to hydrogen dioxide, which in the presence of palladium (free from hydrogen) causes the oxidation.

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[1] Ber. d. deutsch. chem. Gesell. **6**, 106.

Traube also found that indigo-sulphuric acid was only oxidized very slowly by palladium hydrogen, which indicates that ozone is not formed, but only hydrogen dioxide, which has the power of bleaching this coloring matter very slowly. By shaking concentrated or dilute ammonia with palladium hydrogen, hydrogen dioxide was unquestionably formed; but even after the action had continued for twenty minutes, not a trace of nitrous acid could be detected in the solution. These last experiments show that palladium hydrogen with air and water forms only hydrogen dioxide, even in the presence of easily oxidized substances. Traube therefore says that Hoppe-Seyler's hypothesis of the formation of active oxygen has been refuted in all its parts, because he has shown, in the first place, that the chemical processes which take place in animal bodies are essentially different from the phenomena of decay; secondly, that hydrogen is not developed in animal tissues; thirdly, that nascent hydrogen cannot render oxygen active; and finally, that palladium hydrogen at ordinary temperatures does not give off hydrogen, neither has it the power of forming active oxygen or ozone, but in the presence of water it forms with the oxygen hydrogen dioxide alone.

E. H. K.

Analytical Chemistry.

Hydrogen.—A. Tschirikow.[1] It has been shown by W. Hempel[2] that hydrogen is completely absorbed by palladium sponge at 100°, and he has used this as a means of separating hydrogen from a mixture of gases. In order to test the applicability of this property to the estimation of hydrogen evolved in sealed tubes, the author treated zinc with hydrochloric acid in a sealed glass tube containing a palladium spiral. The proportions of acid and zinc were such as to produce a pressure of twenty-five atmospheres if no hydrogen were absorbed by the palladium. The absorption was found to be complete. A small portion of the hydrogen had united with the oxygen of the air remaining in the tube. Nearly the calculated amount of hydrogen was obtained from the palladium spiral by heating to 350°. The evolution of the gas was so regular that the author suggests the heating of palladium-hydrogen as a means of obtaining chemically pure hydrogen.

Chlorine, Bromine and Iodine.—G. Vortmann[3] based a method for the detection and determination of chlorine in the presence of bromine and iodine on the action of superoxides of lead and manganese on chlorides, bromides and iodides in the presence of acetic acid. Iodides are completely decomposed by either. Bromides are decomposed by lead superoxide, but not by the manganese compound. Chlorides are not attacked by either in the presence of acetic acid.

C. L. Müller and G. Kirchler,[4] in commenting on this method, state that chlorine is liberated when chlorides are boiled with superoxide of lead and acetic acid, either absolute or in 50 per cent. or even 10 per cent. solution. Monochloracetic acid is also formed. Chloride of sodium is decomposed by acetic acid and manganese superoxide, but with formation of monochloracetic acid and no free chlorine. By further decomposition, carbon dioxide, water and manganous chloride are formed. Manganese superoxide liberates bromine as well as iodine in presence of acetic acid.

In a subsequent paper[5] Vortmann states that his original reactions hold true when acetic acid of less than 10 per cent. strength is used. It is recommended to use a solution containing only 2–3 per cent. acetic acid. To determine the chlorine in a mixture of chlorides and bromides when the amount of bromides is small, treat with lead superoxide and evaporate to dryness two or three times. When the amount of bromine is large, or when bromides and iodides are both present, either add small portions of lead superoxide to the boiling solution, and boil for half an hour, precipitate the lead with hydrogen sulphide, and evaporate to dryness. Treat the residue with dilute acetic acid and lead superoxide, evaporate again, dissolve the residue in water, and after filtering, precipitate with silver nitrate. Or the iodine may be driven off by evaporating repeatedly with manganese superoxide, then, without filtering, drive off the bromine with superoxide of lead. By the second method the formation of iodic acid is avoided and it is possible to estimate each of the halogens directly.

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[1] J. d. russ. phys.-chem. Gesellsch. 1882, **1**, 47.

[2] Berichte der deutschen chemischen Gesellschaft, **12**, 636.

[3] *Ibid.* **13**, 325. [4] *Ibid.* **15**, 812.

[5] *Ibid.* **15**, 1106; and Monatshefte für Chemie, **3**, 510.

It is very easy to determine bromine in presence of iodine by evaporating the mixture of bromides and iodides several times on a water-bath with manganese superoxide and dilute acetic acid. In order to hasten the separation of the iodine, a moderate stream of air may be passed through the solution.

Sulphur.—C. Winkler[1] has improved the *hydrogen sulphide generator*, previously described by him,[2] which is intended to supply large laboratories. The apparatus consists of two telescoping cylinders of lead. The outer cylinder contains dilute sulphuric acid. The inner one, which contains a shelf for the ferrous sulphide, is suspended by a chain so that it can be raised or lowered in the acid. A stop-cock in the top regulates the escape of the gas. The advantage of the apparatus is that when not in use the inner cylinder is raised out of the acid, so that the gas is not left under pressure, and there is no tendency to leak.

O. Knublauch[3] describes a new method for the estimation of sulphur in illuminating gas. It is a modification of that proposed by Valentin, which as improved by Tieftrunk has been used very generally. In the original method the gas was mixed with air and passed over platinum sponge in a heated platinum tube. The sulphur under these conditions is oxidized to sulphuric acid, which is absorbed in potassium carbonate and determined as barium sulphate. In Knublauch's modification a glass tube heated by a Bunsen burner is substituted for the costly platinum tube, and platinized asbestos is used. The accuracy of the method is increased by using only a slight excess of potassium carbonate, so that the barium sulphate can be washed entirely free from other salts.

For the estimation of sulphurous acid in the air Bernard Proskauer[4] recommends the following. The air to be examined is passed through a solution of potassium permanganate acidified with hydrochloric acid to prevent the formation of potassium hyposulphite. The excess of permanganate is reduced by oxalic acid, and the sulphuric acid resulting from the oxidation of the sulphurous acid is precipitated in the usual way. It is necessary to wash the barium sulphate with hot and moderately strong hydrochloric acid.

L. Leibermann[5] recommends the reaction between sulphurous acid and iodic acid as the best method of detecting the former in wines and other liquids. 15 to 20 cubic centimetres of the liquid are distilled and a few drops of a solution of iodic acid added ; on shaking with chloroform, the violet color, due to iodine liberated by the sulphurous acid, is noticed. If the liquid contains alcohol, water must be added to the distillate to prevent the chloroform from dissolving. For quantitative estimations the wine is distilled until all the alcohol has gone over. The distillate is then diluted with water and treated with hydrochloric acid and barium chloride, to ascertain whether any sulphuric acid has been carried over. If the liquid remains clear it is slightly warmed with concentrated nitric acid in a corked flask. If the amount of sulphurous acid is at all considerable the liquid becomes turbid at once ; if only a trace, the liquid becomes turbid after standing. The reaction of Fordos and Gélis for the detection of sulphurous acid, by reduction to hydrogen sulphide by zinc and hydrochloric acid, may be used in the analysis of wines. But it is better to substitute sodium amalgam for zinc, since the latter frequently contains sulphur.

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[1] Zeitschrift für an. Chem. **21**, 386. [2] *Ibid.* **15**, 285. [3] *Ibid.* **21**, 335.
[4] Zeitschrift für an. Chem. **21**, 443.
[5] Berichte der deutschen chemischen Gesellschaft, **15**, 339.

Hydrogen sulphide may also occur in wines, and it gives the same reaction with iodic acid. It may be detected independently by pouring the distillate from the wine into an alkaline solution of sodium nitro-prussiate. A violet cloud indicates the presence of hydrogen sulphide.

In the estimation of sulphuric acid, Ziegler[1] recommends the addition of silver nitrate after precipitation with barium chloride ; the resulting chloride of silver causes the barium sulphate to settle quickly so that it may be filtered at once. After washing the precipitate with water the chloride of silver may be removed by ammonia.

G. Lunge[2] recommends the use of nitric acid of specific gravity 1.42, mixed with one-third its volume of strong hydrochloric acid, for the purpose of dissolving iron pyrites. This mixture attacks the mineral much more actively than nitric acid of specific gravity 1.48.

Nitrogen.—As a sensitive test for gaseous ammonia G. Kroupa[3] recommends the use of papers saturated with fuchsine solution made yellow with sulphuric acid. They turn red with ammonia.

The ordinary method for estimating ammonia, by distilling into a receiver containing a standard solution of an acid, is open to the objection that, by irregular absorption of the ammonia, the acid occasionally runs back into the distilling flask. O. Knublauch[4] has arranged a receiver which is intended to avoid this difficulty. The ammonia is distilled from an ordinary flask through a glass tube connected by a rubber stopper with a glass cylinder about 40 mm. wide and open at the bottom. This dips under the surface of the standard acid contained in a beaker. The entire receiver is placed in a jar containing water that is kept cold. By this arrangement air enters the cylinder whenever there is a tendency for the liquid to rush back toward the flask. The flask is heated rapidly from the beginning; after distilling off ½ to ⅔ of the liquid the glass tube is disconnected and the excess of acid titrated directly in the absorption cylinder. The method is applicable for estimating large or small quantities of ammonia and gives accurate results.

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[1] Berichte der deutschen chemischen Gesellschaft, **15**, 262.

[2] *Ibid.* **15**, 1091.

[3] *Ibid.* **15**, 88.

[4] Zeit. an. Chem. **21**, 161.

A. Jorissen[1] proposes to use the reaction, discovered by Vogel,[2] of nitrous acid on an alcoholic solution of rosaniline or fuchsine as a test for nitrous acid. It is best to use fuchsine in glacial acetic acid solution, instead of an alcoholic solution. 0.01 gram of fuchsine is dissolved in 100 cc. glacial acetic acid, and to two cubic centimetres of this solution a few drops of the liquid are added in a porcelain dish. If nitrous acid is present the liquid becomes violet, then blue, then green, and finally yellow. If a free mineral acid is added the mixture becomes yellow finally, but on adding water the original color of the fuchsine is reproduced, which is not the case when nitrous acid is present.

E. W. Davy[3] describes a new and expeditious method for the determination of nitrites. When an aqueous solution of gallic acid is treated with a solution of nitrous acid or a nitrite, a yellowish brown coloration results. If the amount of nitrous acid is very small the reaction is hastened by heat. One part of nitrous acid in twenty million parts of water has been detected by the author. The intensity of the color being proportional to the amount of nitrite, the method can be used for quantitative estimations in a manner analogous to the determinations of ammonia by Nessler's solution. The reaction is said to be nearly as delicate as the phenylene di-amine reaction of Griess.

W. Hempel[4] has investigated the methods for the preparation and analysis of nitrous oxide, and finds that Bunsen's method of analysis by exploding with hydrogen and a detonating mixture of hydrogen and oxygen, is undoubtedly the best. A mixture of 100 parts nitrous oxide with 460 parts hydrogen will not explode, whereas a mixture of 100 parts nitrous oxide with 116 parts hydrogen explodes with violence. The most favorable conditions for the analysis are to add to the nitrous oxide, two or three times its volume of hydrogen, and, in mixtures of nitrous oxide with other gases, 26 to 64 volumes of the detonating mixture to 100 volumes of non-combustible gas. The anomalous results formerly obtained with this method have been due in great measure to the difficulty in obtaining the gas in chemically pure condition. The author has not been able to prepare the gas purer than 98.8 per cent. N_2O. A small quantity of nitrogen is always present.

C. Böhmer[5] recommends the use of potassium permanganate and chromic acid as absorbents for nitric oxide. A saturated solution of potassium permanganate in water absorbs nitric oxide equally as well as ferrous sulphate, and has the advantage that, when used in alkaline solution, carbonic acid can be absorbed at the same time. The absorption results in oxidation of the nitric oxide to nitric acid. It is aided by warming, and by its use many estimations of amido compounds, according to the method of Sachsse and Kormann, can be made in a day. If it is not required to absorb carbonic acid, chromic acid gives still better results. 1 cc. of a solution of 50 grams in 100 cubic centimetres of dilute nitric acid will absorb 18 cc. of nitric oxide rapidly.

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[1] Zeitsch. an. Chem. **21**, 210.

[2] Journ. prak. Chem. **94**, 457.

[3] Chemical News, **46**, 1.

[4] Berichte der deutschen chemischen Gesellschaft, **15**, 903.

[5] Zeitschrift f. an. Chem. **21**, 212.

W. Bettel[1] states that after removing nitrates by the copper zinc couple, the total organic nitrogen in a given solution may be estimated as ammonia (after removing free ammonia, and that from the decomposition of the nitrates) by evaporation with pure caustic soda in a copper flask of peculiar construction, finally evaporating to dryness and igniting, adding water and redistilling. When cyanides are formed on ignition, sufficient potassium permanganate is added to oxidize to cyanates. These, on adding water and boiling, are converted into ammonia.

Phosphoric Acid.—Zimmerman[2] proposed a modification of the Margueritte method for determining ferrous salts volumetrically by means of a standard solution of potassium permanganate. This modification consists in adding a solution of manganous sulphate to the ferrous solution to be determined when the latter contains hydrochloric acid. The manganous sulphate effectually prevents liberation of chlorine due to the oxidation of hydrochloric acid by the permanganate. Errors due to chlorine are thus avoided. Von der Pfordten[3] now applies the principle of the method as modified by Zimmerman to the determination first of molybdic and then of phosphoric acid.

Molybdic acid is determined as follows: The salt to be analyzed is dissolved in a little water, to which 60 cc. of a 27 per cent. hydrochloric acid solution are added. 8 to 10 grams of zinc in the form of sticks (the amount of iron in which has previously been determined by titration) are then introduced. When the solution has become yellow, which often results without heating, the flask is cooled before all the zinc has been dissolved, and the contents are transferred to a porcelain dish containing water, dilute sulphuric acid and manganous sulphate. (The latter salt solution is prepared by dissolving 100 grams of manganous sulphate in water and diluting to 500 cc.; 20 cc. of this solution are sufficient to prevent evolution of chlorine from 50 cc. of hydrochloric acid of specific gravity 1.12.) Potassium permanganate is now added by means of a pipette, stirring actively towards the end of the reaction, which is indicated by the appearance of a rose color. The final product of the reduction of molybdic acid is not the sesquioxide, M_2O_3, but a suboxide, which, however, by contact with the air is quickly oxidized to the sesquioxide, and, unless the air is excluded, the latter is the result of reduction.

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[1] Chemical News, **45**, 38.

[2] Berichte der deutschen chemischen Gesellschaft, **15**, 929.

[3] Annalen der Chemie, **213**, 314.

Phosphoric acid is determined as follows: The precipitate of ammonium phospho-molybdate is obtained in the usual way, and washed free from molybdic acid by means of a nearly saturated solution of ammonium sulphate. It is then dissolved in ammonia and diluted to a definite volume, of which a measured volume is taken which must not contain more than 0.3 gram MoO_3. Zinc and hydrochloric acid are used for reduction as above described for molybdic acid. From the amount of permanganate used the molybdic acid is determined, and from the latter the phosphoric acid by the relation $24MoO_3$ to $1P_2O_5$,

1 cc. $KMnO_4 = 0.0007585$ Oxygen
1 cc. " $= 0.004551$ MoO_3
1 cc. " $= 0.0001869$ P_2O_5

Good results were obtained by this method, which is applicable in all cases in which the separation of phosphoric acid by means of ammonium molybdate can take place.

D. T. D.

NOTES.

Atomic Weight of Thorium.

NILSON[1] has prepared pure thoria and metallic thorium, and redetermined some of their properties. The sp. g. of the metal ranges from 10.9901 to 11.0102 at 17°; which gives it a molecular volume almost exactly equal to the molecular volumes of Zr, Ce, La, and Di. It was obtained as a grey powder consisting of microscopic crystals. The oxide, ThO_2, has a sp. g. of 10.22 at 17°. These figures are much higher than those given by previous experimenters.

The atomic weight of thorium was determined from analyses of the sulphate. The crystallized salt, $Th(SO_4)_2, 9H_2O$, gave the following percentages of thoria upon ignition:

45.097
45.092
45.081
45.086
45.088
45.099

Mean, 45.0905

Hence, if $O = 16$ and $S = 32$, $Th = 232.43$.

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[1] Ber d. deutsch. chem. Gesell. **15**, 2519-2547.

The anhydrous sulphate gave these percentages of ThO_2:

	62.300
	62.298
	62.294
	62.298
Mean,	62.2975

Hence, Th = 232.37.

If we recalculate these data with the value for O and S given in my recent pamphlet on atomic weights, O = 15.9633; ± .0035, and S = 31.984; ± .012, they lead to the subjoined results:

From the hydrated salt,	$ThO_2 = 263.941; \pm .0394$
" " anhydrous salt,	" $= 263.959; \pm .0531$
General mean,	$ThO_2 = 263.947; \pm .0316$

Hence, Th = 232.020; ± .0323.

The general mean obtained by combining all the results of Berzelius, Hermann, Chydenius, Delafontaine, and Cleve, which differed inappreciably from Cleve's results taken alone, was Th = 233.414; ± .0725. It will be seen that Nilson's figures give a value having a much lower probable error, and that the new figure is therefore entitled to relatively very high credit. The general mean of all, including Nilson's, is Th = 232.262; ± .030.

F. W. Clarke.

Synthesis of Uric Acid.

Horbaczewski has succeeeded in effecting the synthesis of uric acid in the following way: Pure, finely powdered glycocol, obtained from hippuric acid, was mixed with ten times its weight of pure urea, prepared from ammonium cyanate, and quickly heated to 200–230° C. in a flask placed in a metal bath, this temperature being maintained until the fused mass, originally perfectly colorless and clear, became brownish yellow, turbid and viscid. After cooling the mass was dissolved in potassium hydroxide, the solution supersaturated with ammonium chloride, and precipitated with a mixture of an ammoniacal solution of silver and magnesia. The precipitate, which contained the uric acid, was well washed with ammoniacal water and decomposed with potassium sulphide. After the precipitate was filtered off, the filtrate was saturated with hydrochloric acid and concentrated. The product which separated on cooling was re-dissolved in dilute potassium hydroxide and twice again subjected to the same treatment. Finally there was obtained a yellowish colored crystalline powder, which was first washed with alcohol, then dried, afterward treated with carbon bisulphide to remove sulphur, and finally treated with ether. The substance purified in this way showed all the properties and reactions of uric acid. The combustion gave results agreeing with the formula of the acid.[1]—(*Berichte der deutsch. chem. Gesellschaft*, **15**, 2678.)

The Use of Liquid Carbon Dioxide.

A. W. HOFMANN has called attention to the extensive use of liquid carbon dioxide for various purposes. The gas is condensed and sold by F. A. Krupp of the world renowned iron works in Germany. It is used mostly to compress steel castings in closed molds. It is placed in wrought steel vessels which hold 100 kilos of the liquefied gas. A pressure of 800 atmospheres is obtained. In Krupp's works all the ice is manufactured with the aid of a machine which is kept constantly at work by compressed carbon dioxide. A large quantity of soda water used in the same works is made from liquid carbon dioxide. One of the most interesting applications of the compressed gas has been recently made in Berlin in connection with fire engines. Each engine is supplied with a large vessel containing the liquid. This is brought into use as a motor the instant the engine arrives at the place of the fire, and some of the gas is thrown with the water upon the flames. As soon as sufficient pressure of steam is obtained, the use of the carbon dioxide is stopped.—(*Berichte der deutsch. chem. Gesellschaft*, **15**, 2668.)

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[1] The action of urea on glycocol at the temperature of fusion has been studied by Griess (Berichte der deutschen chemischen Gesellschaft, **2**, 106), who obtained an acid of the formula $C_3H_6N_2O_3$:

$$C_2H_5NO_2 + CH_4N_2O = C_3H_6N_2O_3 + NH_3.$$

It is, of course, possible that, at the high temperature at which Horbaczewski operated, uric acid may be formed; but, even conceding this, any rational interpretation of the reaction would be impossible, as it certainly is without analogy. The details will be awaited with impatience.
I. R.

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V. RENTELN. Beiträge zur forensischen Chemie des Solanins.

LEIPZIG.

BEYER, B. Uber einige Derivate der Isophtalsäure.

F. W. C

VOL. IV. [MARCH, 1883.] NO. 6.

AMERICAN

CHEMICAL JOURNAL.

EXPERIMENTS ON THE GASES OCCLUDED BY COKE.

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No small amount of labor has been expended by chemists in studying the amount and character of the gases held confined by porous solids. Professor Reichardt,[1] of Jena, in particular, and his pupils have published several important papers upon the subject, and many observers have experimented, more or less carefully, upon the gases contained in charcoal, coke, and coal.

With the view of gaining a clearer comprehension of the significance of Reichardt's method of working than was possible from merely reading the memoirs which relate to it, we have performed a number of experiments somewhat similar to his. We have moreover worked in a critical spirit, with the utmost care, and with attention specially directed to a just appreciation of the limitations of such experiments and to the sources of error with which they are beset. The method employed by Reichardt and his disciples was to fill with quicksilver the vessel which contained the substance to be examined, and so expel the air from the vessel, as well as from the interstices between the particles of the substance. The arrangement of the apparatus and the precautions to be observed in using it will be found in Fresenius's Zeitschrift für analytische Chemie, 1868, **7**, 184. The charged flask was heated in a paraffin bath to 140° or 200° as long as gases were evolved, and at the conclusion of the experiment a new portion of mercury was allowed to flow into the flask, in order to push out, through the delivery tube, the last portions of gas which had been expelled from the substance by heating. We have ourselves found a Berlin flask of 75 to 100 cc. capacity well suited for use in this connection, and that 20 grams of pulverized coke was a sufficient quantity of material. From this amount of coke we commonly obtained from 15 to 20 cc. of gases.

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[1] See Reichardt & Blumtritt, Liebig & Kopp's Jahresbericht, 1866, p. 53; Doebrich, *ibid.* 1868, p. 946; Scheermesser, *ibid.* 1871, p. 1059.

As will be seen on examining the experiments recorded below, we have repeatedly tested the value of the foregoing method, by comparing the gases obtained by means of it with those got by heating similar samples of coke in a vacuum obtained by means of the Sprengel pump. The results of our trials go to prove that Reichardt's method has merit in so far as it goes; that is to say, a considerable portion of the occluded gases can be expelled by means of it. The results hitherto published by Reichardt and his pupils, as obtained in this way, are undoubtedly valuable; though, as would naturally be expected, the method is less effective than the one based on working in a vacuum. It is manifest, moreover, that even when the Sprengel pump is used, the temperatures of 200°, and less, at which most of our experiments were performed, are not high enough for the complete expulsion of the gases occluded by coke.

Our Sprengel pump was of the form described by S. W. Johnson[1] and E. H. Jenkins. For analyzing the gases obtained from the cokes we employed the apparatus of Doyère as modified by Hinman,[2] which admits of the measurements being made at a constant pressure and temperature. The gases were estimated in the usual way, viz. carbonic acid by absorption with strong potash lye; oxygen by absorption with alkaline pyrogallate of potash, and carbonic oxide by exploding with oxygen admixed with hydrogen and absorbing the resulting carbonic acid with potash lye. Nitrogen was estimated by the difference. It was evident that little if any hydrogen was contained in the gases examined by us. We were never able to explode any sample of the gas with oxygen alone; nor did we notice any appreciable contraction of the original volume on exploding after addition of a mixture of oxygen and hydrogen. This apparent absence of hydrogen is a point which needs to be carefully studied. We have postponed the consideration of it, since it seemed to have no immediate bearing on the comparisons we were actually making.

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[1] This Journal, 1880, **2**, 29.

[2] American Journal of Science, 1874, **8**, 182.

When no mention is made of other gases than carbonic acid and oxygen in the following description of details, it is to be understood that the analysis was carried no further, and that no effort was made to determine carbonic oxide or hydrogen in those special cases. On the other hand, in every instance where the amount of nitrogen is recorded, the presence or absence of carbonic oxide was proved.

All the cokes examined by us were from the Boston Gas Light Company. They were well burnt, as the term is, *i. e.* thoroughly deprived of illuminating gas. The custom at the works is to keep each charge of coal in its retort during four hours at a temperature not far from 2000° F.[1] The retorts are of clay 9′×15″×26″, and they are worked in connection with exhausters which reduce the pressure within them to the value of a column of water a quarter inch in height.

SERIES I.—*Air-Dried Coke from a Dwelling-house.*

We first examined some coke which had lain nearly a year in the dry cellar of a dwelling-house. A powdered portion of it gave off 2.7 per cent. of moisture when heated for an hour and a half at 110° in an air-bath. It may here be said that in most instances the cokes examined by us were powdered finely enough to pass through a sieve the orifices of which were one millimetre in diameter. In three instances, however, viz. in Exps. B, C, and Z, the holes of the sieve were two millimetres wide. Twenty grams of the finer coke compacted rather firmly in a measuring cylinder occupied a space of 30 cubic centimetres.

Three separate portions of the coke were heated at different times according to Reichardt's method in a paraffin bath, with the following results:

A. 22 grams of the coke were taken. On heating for half an hour at 80° C. no gas was obtained. During the next half-hour at

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[1] According to determinations made by me, on the assumption that the specific heat of wrought iron is 0.126 at this temperature.—D. S. LEWIS.

100° rather more than 4 cc. of gas came off; during the next 15 minutes at 120° about 5 cc. were obtained, and during the next hour, at 150°, 6 or 7 cc. In the gas obtained up to 150° there was found 31.09 per cent. of carbonic acid and 25.39 per cent. of oxygen, some of which came, of course, from air that was loosely entangled by the coke and had not been completely expelled when the flask was filled with the mercury. The same coke was heated further for half an hour at 180°, when 4 cc. more of gas came off, and for an hour and twenty minutes at 200°, when 4 cc. or so of gas were obtained. This gas obtained between 150° and 200° was found to contain 65.60 per cent. of carbonic acid, but the amount of oxygen in it was too small to measure.

In brief, the 22 grams of coke (A) heated to 200° gave in all 22½ cc. of gas (accurately measured[1]), which contained 43.03 per cent. of carbonic acid and a very considerable amount of oxygen, as well as nitrogen.

B. 13 grams of the coke somewhat coarser than the preceding sample, heated 30 minutes at 100°, gave about 6 cc. of gas; 15 minutes at 120° about 4 cc.; one hour at 150° about 4 cc.; and one hour at 200° 2 cc. Accurately measured, 13 grams of the coke heated to 200° gave 15 cc. of gas which contained 41.43 per cent. of carbonic acid, 5.74 per cent. of oxygen, and 52.83 per cent. of nitrogen.

C. 19 grams of the coke similar to B, heated 15 minutes to 100°, gave about 8 cc. of gas, for one hour at 150° 8 cc. and for one hour at 200° rather more than 5 cc., or all told, 19 grams of coke heated to 200° gave 22 cc. of gas which contained 42.50 per cent. of carbonic acid, 6.49 per cent. of oxygen, and 51.01 per cent. of nitrogen.

The five following samples (D to H) of the same air-dried coke were heated in a paraffin bath, as before, but the flask which contained the coke was now connected with a Sprengel pump, by means of which the air originally contained in the flask and that entangled by the particles of coke was removed in the first place before the flask was heated. A vacuum was of course maintained throughout the experiment, *i. e.* the pump was kept in action to facilitate the escape of the gases from the coke and to remove them from the flask immediately.

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[1] It is to be understood that in many instances the amounts of gas obtained at the intermediate temperatures were estimated roughly, *i. e.* without any attempt at accurate measurement. The final measurements, and all those upon which the analyses depended, were of course made with the most scrupulous care.

D. 21 grams of the coke were taken. The air exhausted from the flask before heating was found to contain 0.19 per cent. of carbonic acid and 19.77 per cent. of oxygen.[1] On heating the coke to 75° only a small quantity of gas came off. On heating half an hour at 100° about 5 cc. of gas were obtained; for 45 minutes at 150° 3 cc., and for one hour at 200° 6 or 8 cc. more. In all, the 21 grams coke heated to 200° in connection with the Sprengel pump gave 17 cc. of gas, which contained 62.97 per cent. of carbonic acid, 5.31 per cent. of oxygen, and 31.72 per cent. of nitrogen.

E. 40 grams of the coke were taken, and the apparatus was exhausted of air at the ordinary temperature. On subsequently heating one hour at 100° 12½ cc. of gas were collected; which, on analysis, was found to contain 41.97 per cent. of carbonic acid, 11.72 per cent. of oxygen, 1.45 per cent. of carbonic oxide, and 44.86 per cent. of nitrogen. On heating one hour longer at 200° 17½ cc. more of gas came forward which contained 57.48 per cent. of carbonic acid, 3.25 per cent. of oxygen, 4.97 per cent. of carbonic oxide, and 34.30 per cent. of nitrogen. The total 30 cc. of gas obtained by heating the 40 grams of coke to 200° contained 51.03 per cent. of carbonic acid, 6.77 per cent. of oxygen, 3.50 per cent. of carbonic oxide, and 38.70 per cent. nitrogen.

F. 41 grams of the coke were placed in the flask, and in order to try whether the material could be completely freed from entangled air, there was carried to the bottom of the coke a tube through which purified nitrogen gas was forced during half an hour, at the ordinary temperature and pressure of the air. This nitrogen was proved by analysis to contain neither oxygen nor carbonic acid before it was admitted to the flask. On testing, at the close of the half-hour, the gas which had come forward, it was found to contain 5.28 per cent. of oxygen, but no carbonic acid. The pure nitrogen was passed through the coke during a second half-hour, and was then found to be free from both oxygen and carbonic acid. The apparatus was now left to stand for a day and a half full of the pure nitrogen, and at the end of this time a current of the nitrogen was passed through the coke during twenty minutes, but on testing the outcoming nitrogen neither oxygen nor carbonic acid was detected, at least not in measurable quantities. After the nitrogen had been pumped out of the flask the latter was heated for an hour at 100° ; 10½ cc. of gas came forward, which contained 35.26 per cent. carbonic acid, 5.40 per cent. oxygen, 2.84 per cent. carbonic oxide, and 56.50 per cent. nitrogen. On heating during another hour at 200° 16½ cc. of gas came off, the composition of which was 79.93 per cent. carbonic acid, 0.3 per cent. oxygen, 4.22 per cent. carbonic oxide, and 15.55 per cent. nitrogen. In all, the 41 grams coke yielded 27 cc. of gas when heated up to 200°, and the gas contained 62.57 per cent. of carbonic acid, 2.29 per cent. oxygen, 3.69 per cent. carbonic oxide, and 31.45 per cent. nitrogen.

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[1] In another experiment, the air exhausted from a flask containing 24 grams of this kind of coke was found to contain 0.4 per cent. carbonic acid, 20.77 per cent. oxygen, and 78.83 per cent. nitrogen.

G. 20 grams of the coke were treated with the purified nitrogen, as in F, during two half-hour terms, and the outcoming gas was proved to be free from oxygen and carbonic acid. The Sprengel pump was then set in action for 15 minutes, and the gas thus obtained was tested. A trace of oxygen, but no carbonic acid, was found in it. The coke was then heated for an hour at 100° and 11 cc. of gas were obtained, which contained 25.53 per cent. carbonic acid, 6.27 per cent. oxygen, 0.46 per cent. carbonic oxide, and 67.74 per cent. nitrogen. On heating during another hour at 200° 16¼ cc. of gas were obtained, which contained 68.78 per cent. carbonic acid, 2.54 per cent. oxygen, 0.68 per cent. carbonic oxide, and 28.00 per cent. nitrogen. In all, the 20 grams coke heated to 200° gave 27¼ cc. gas, which contained 51.46 per cent. carbonic acid, 4.06 per cent. oxygen, 0.59 per cent. carbonic oxide, and 43.89 per cent. nitrogen.

H. 18 grams of the coke were treated with nitrogen, as in G, for half an hour at the ordinary pressure of the air, at the end of which time neither oxygen nor carbonic acid was found in the outcoming gas. The pump was then put in action, and traces of both oxygen and carbonic acid were detected in the gas thus obtained. The apparatus full of nitrogen was left at rest for a day and a half and then exhausted at the ordinary temperature. The 79 cc. of gas examined contained 0.59 per cent. carbonic acid and 5.53 per cent. oxygen. The pump being kept in action, the coke was heated one hour to 100° and 5¼ cc. of gas were obtained, which contained 33.08 per cent. of carbonic acid, 6.15 per cent. oxygen, 0.96 per cent. carbonic oxide, and 59.81 per cent. nitrogen. On heating during another hour to 200° 10 cc. of gas were obtained, which contained 76.25 per cent. carbonic acid and 0.5 per cent. oxygen. The other constituents were not determined. In all, the 18 grams coke heated to 200° gave 15¼ cc. of gas which contained

61.50 per cent. carbonic acid and 2.43 per cent. oxygen, as well as some carbonic oxide and nitrogen.

SERIES II.—*Air-Dried Coke from Store-house.*

This coke had been lying two years in a dry store-house at the gas works in Boston.

I. 24 grams of the coke heated in Reichardt's manner during 15 minutes at 100° gave some 10 cc. of gas; for 30 minutes at 150°, 10 cc., and for one hour at 200°, 9 cc. In all, 29 cc. of gas, which contained 32.75 per cent. carbonic acid, 8.21 per cent. oxygen, and 59.04 per cent. nitrogen.

J. 25 grams of the coke were put in a flask and the air was exhausted, at the ordinary temperature, with the Sprengel pump. It was found to contain 0.09 per cent. carbonic acid and 20.15 per cent. oxygen. On heating the coke for half an hour at 100°, about 4 cc. of gas were obtained; for 45 minutes at 150°, 3 or 4 cc., and for an hour and a half at 200°, 5 or 6 cc. In all, 14¾ cc. which contained 61.37 per cent. carbonic acid, 4.82 per cent. oxygen, and 33.81 per cent. nitrogen.

K. 44 grams of the coke were put in a flask into which some recently boiled and cooled water was poured, and the apparatus was connected with the Sprengel pump and exhausted. On heating an hour and a half at 100°, some 4 cc. of gas were obtained, which contained 11.46 per cent. carbonic acid, 3.66 per cent. oxygen, and 84.88 per cent. nitrogen. On heating an hour at 200°, 20⅓ cc. of gas were obtained, which contained 76.32 per cent. carbonic acid and 0.44 per cent. oxygen. In all, the 44 grams coke heated to 200° gave 24⅓ cc. gas, which contained 65.42 per cent. carbonic acid and 0.98 per cent. oxygen, besides nitrogen.

L. 21 grams of the coke were placed in a flask, and nitrogen gas of assured purity was passed through it during 45 minutes; the pump was also filled with the nitrogen, and the whole apparatus was left at rest for four days at the pressure of the air. Under these conditions it appeared that a little carbonic acid and oxygen diffused out from the coke into the nitrogen gas, for on exhausting the apparatus and analyzing the 67½ cc. of "nitrogen" obtained, it was found to contain 1.11 per cent. carbonic acid and 1.88 per cent. oxygen. On subsequently heating the coke for one hour at 100°, and another hour at 200°, 17¼ cc. of gas were obtained, which contained 64.68 per cent. carbonic acid and 0.41 per cent. oxygen.

M. 41 grams of the coke were put in a flask and a current of pure nitrogen gas was passed through it for 45 minutes at the ordinary temperature and pressure. The outcoming gas was found to be free from carbonic acid and oxygen. The Sprengel pump was then connected with the flask and filled with the nitrogen, and the apparatus was left at rest during four days at a pressure slightly less than that of the atmosphere. On then exhausting the flask 26 cc. of the "nitrogen" were collected for examination. It contained 1.28 per cent. carbonic acid and 2.40 per cent. oxygen. On heating the coke to 100° for an hour, 6 cc. of gas were obtained, which contained 56.26 per cent. carbonic acid, 1.2 per cent. oxygen, and 42.54 per cent. nitrogen. On heating during another hour at 200°, 21 cc. of gas were obtained, which contained 79.66 per cent. carbonic acid, 0.19 per cent. oxygen, 1.55 per cent. carbonic oxide, and 18.60 per cent. nitrogen. In all, the 41 grams of coke heated to 200° gave 27 cc. of gas, which contained 74.51 per cent. carbonic acid, 0.42 per cent. oxygen, 1.21 per cent. carbonic oxide, and 23.86 per cent. nitrogen.

SERIES III.—*Old Coke, from out-of-doors.*

This coke had been left in a heap exposed to the weather for three years or more in a storage yard a mile or two from the gas works.

N. 22 grams of the coke heated, in Reichardt's manner, one hour at 200° gave 22 cc. of gas, which contained 28.31 per cent. carbonic acid, 9.02 per cent. oxygen, and 62.67 per cent. nitrogen.

O. 23 grams of the coke were taken, air was exhausted from the flask with the Sprengel pump, and the coke was then heated one hour at 200°; 9½ cc. of gas were obtained, which contained 54.66 per cent. carbonic acid and 4.29 per cent. oxygen, besides nitrogen.

P. 23 grams of the coke having been placed in a flask, recently boiled and cooled water was added and the air exhausted at the ordinary temperature. On then heating the coke one hour at 100° 3 cc. of gas were obtained, which contained 6.65 per cent. carbonic acid and 6.01 per cent. oxygen, besides nitrogen. On heating for another hour at 200° 6½ cc. of gas came forward, which contained 74.27 per cent. carbonic acid and 0.31 per cent. oxygen, besides nitrogen. In all, 23 grams of coke gave 9½ cc. of gas containing 52.22 per cent. carbonic acid and 2.17 per cent. oxygen.

Q. 45 grams of coke were put in a flask, cooled boiled water was added and the apparatus was exhausted at the ordinary temperature. On then heating the coke one hour at 100° 5¾ cc. of gas were obtained, which contained, besides nitrogen, 17.31 per cent. carbonic acid and 1.05 per cent. oxygen. On heating during another hour at 200° 12 cc. of gas were obtained, which contained 67.57 per cent. carbonic acid and 2.70 per cent. oxygen. In all, the 45 grams coke gave 17¾ cc. of gas containing 51.22 per cent. carbonic acid and 2.16 per cent. oxygen.

In another trial, water was boiled directly in the flask, and after it had cooled, 22 grams of coke were added, the Sprengel pump was connected and the apparatus exhausted. On heating the coke for half an hour to 80° 1 cc. of gas came off, for an hour and twenty minutes longer at 80° half a cc., for half an hour at 100° half a cc., for half an hour up to 200° 2 cc., and for another half-hour at 200° half a cc.; accurately measured, the 22 grams of coke heated to 200° gave 5⅓ cc. gas which contained 18.06 per cent. carbonic acid, 1.49 per cent. oxygen, and 80.45 per cent. nitrogen. We are unable to account for the lack of accordance between these results and those obtained in experiments P and Q.

R. 39 grams of the coke were put in a flask, the apparatus was exhausted and left to stand two days and a half at the ordinary temperature. On then pumping anew, without any application of heat, 4 cc. of gas were obtained which contained 8.65 per cent. carbonic acid, 12.74 per cent. oxygen, and 78.61 per cent. nitrogen. On now heating to 100° for one hour 5½ cc. gas were obtained, which contained 57.64 per cent. carbonic acid, 3.13 per cent. oxygen, and 39.23 per cent. nitrogen. On heating to 200° during another hour 7⅓ cc. of gas were obtained, which contained 75.96 per cent. carbonic acid, no oxygen (!), 0.68 per cent. carbonic oxide, and 23.36 per cent. nitrogen. In all, the 39 grams of coke heated to 200° gave nearly 17 cc. of gas which contained 53.52 per cent. carbonic acid, 4.14 per cent. oxygen, 0.39 per cent. carbonic oxide, and 41.95 per cent. nitrogen.

S. 42 grams of the coke were put in a flask, and pure nitrogen gas was passed through it for half an hour at the ordinary temperature and pressure, when a sample of the outcoming gas was collected for analysis. It contained no oxygen, but 2.35 per cent. of carbonic acid. Nitrogen was passed through the coke during another half-hour, and a sample then taken was found to contain no oxygen, as before, and 1.41 per cent. carbonic acid. The nitrogen was passed through the coke yet another half-hour, when the flask was put in connection with the pump and exhausted of its gaseous contents. On then heating the coke to 100° for one hour 10 cc. of gas were obtained, which contained 47.18 per cent. carbonic acid and 1.11 per cent. oxygen. On heating to 200° during another hour 13¾ cc. of gas were collected, which contained 70.63 per cent. carbonic acid and a third of a per cent. of oxygen. In all, the 42 grams of coke heated to 200° gave 23¾ cc. of gas, which contained 60.78 per cent. carbonic acid and 1.10 per cent. oxygen, besides nitrogen. It appeared in this case that by using nitrogen gas to clear out the flask the oxygen entangled by the coke was removed more completely than could be done in the case of the thoroughly air-dried coke of Exps. F, G, and H. We are ignorant as to whether this fact is in any way connected with the presence of the larger proportion of moisture which was contained in the coke which had lain out-of-doors, but that this old coke differed decidedly in some way from the other cokes examined by us is shown by the circumstance that it gave up a smaller proportion of carbonic acid than any of the other cokes, excepting the one taken directly from a gas retort. It will be of interest to determine whether, generally speaking, other specimens of old, weathered coke contain a correspondingly small proportion of carbonic acid, for the fact might possibly have some influence on the kindling temperature of the material. A somewhat similar remark is suggested by the small amount of carbonic acid obtained in Experiments Y, Z, and AA (beyond), from coke taken directly from a gas retort and cooled without wetting. It has been noticed in Boston that many people who habitually use coke as fuel prefer that which has lain in the storage yards, though the reason of this preference may be that some sulphur has been eliminated from the coke by the weathering, and perhaps that the coke is less thoroughly saturated with water than that delivered directly from the gas works immediately after it has been quenched. It would be hard to judge, without further investigation, as to the bearings upon this question of De Saussure's[1] observations that charcoal absorbs much less carbonic acid when wet than when dry, and that dry charcoal charged with carbonic acid gives up a considerable part of the gas when wetted.

SERIES IV.—*Recent, partially-dried Coke.*

This coke had been made about a fortnight before our examination of it. After having been quenched with water in the usual way, it had been carried to a storage yard and left there under a roof, *i. e.* in a shed open at the sides.

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[1] Gilbert's Annalen der Physik, 1814, **47**, 120.

T. 21 grams of the coke heated in Reichardt's manner during fifteen minutes at 100° gave some 12 cc. of gas, heated thirty minutes at 150° it gave 6 cc., and for an hour at 200° about 4 cc. In all, the 21 grams of coke heated to 200° gave 22⅔ cc. gas, and the gas contained 32.45 per cent. carbonic acid, 1.81 per cent. oxygen, 4 per cent. carbonic oxide, and 61.74 per cent. nitrogen.

U. 21 grams of the coke were put in a flask, which was then exhausted with the Sprengel pump at the ordinary temperature. On heating the coke up to 150° 3 cc. of gas were collected, and on heating half an hour at 200° 6 cc. came forward. In all, the 21 grams coke gave 9 cc. of gas, which contained 72.45 per cent. carbonic acid and 2.33 per cent. oxygen.

V. 22 grams of the coke treated similarly to that of the foregoing experiment (U), but heated immediately to 200° and maintained at that temperature during three hours, gave 12¾ cc. of gas, which contained 73.01 per cent. carbonic acid, 1.57 per cent. oxygen, and 25.42 per cent. nitrogen.

W. 39 grams of the coke were allowed to stand at the ordinary temperature during four days in a flask from which the air had been exhausted. On again exhausting the flask 3½ cc. of gas were obtained, which contained 5.95 per cent. carbonic acid, 5.38 per cent. oxygen, and 88.67 per cent. nitrogen. On then proceeding to heat the flask to 100° for an hour, 6¼ cc. of gas were obtained, which contained 97.93 per cent. carbonic acid, and so little of other ingredients, besides nitrogen, that the amounts of them could not be measured. On heating to 200° for an hour 14¾ cc. of gas were obtained, which contained 82.58 per cent. carbonic acid, 1.49 per cent. oxygen, 2.23 per cent. carbonic oxide, and 13.70 per cent. nitrogen. In all, there were obtained from the 39 grams coke up to 200° 24½ cc. gas which contained 75.5 per cent. of carbonic acid. The 21 cc. gas obtained by actually heating, first to 100° and then to 200°, contained 87.16 per cent. carbonic acid.

X. 26 grams coke were kept in an exhausted tube of hard glass for 2½ days at the ordinary temperature of the air; nearly 5½ cc. of gas were obtained, which contained 8.29 per cent. carbonic acid, 16.02 oxygen, and 75.69 per cent. nitrogen. On then heating the tube to low redness for 20 minutes some 35 cc. of gas were obtained, which was evidently nearly all that could be expelled from the coke at that temperature. On analysis, the gas was found to contain 78.47 per cent. carbonic acid and 0.55 per cent. oxygen. An accident prevented the determination of the other constituents of the sample. On heating the tube 20 minutes longer, to intense redness, 40 cc. more of gas came forward, and still more might have been obtained had not the tube cracked. The gases obtained at the ordinary temperature and at low redness, taken together, contained 62.37 per cent. carbonic acid and 4.10 per cent. oxygen. There were 40½ cc. of this gas, let alone the 40 cc. obtained at the higher temperature.

SERIES V.—*Coke taken immediately from a Gas Retort.*

The coal from which this coke was obtained had been heated in one of the ordinary gas retorts at the works during four hours in the usual way. The coke drawn from the retort in a state of ignition was not wetted, but was cooled in closed vessels expressly for our experiments.

Y. 24 grams of the coke heated, in Reichardt's manner, for 15 minutes at 100° gave some 10 cc. of gas, for 30 minutes at 150° about 10 or 12 cc. more, and for one hour at 200° about 10 cc. more. In all, the 24 grams coke heated to 200° gave 33 cc. gas, which contained 7.36 per cent. carbonic acid, 5.10 per cent. oxygen, and 87.54 per cent. nitrogen.

Z. 14 grams of the coke heated, in Reichardt's manner, for 15 minutes at 100° gave 5 cc. of gas, for 30 minutes at 150° 6 or 7 cc., and for one hour at 200° 5 or 6 cc. In all, the 14 grams of coke heated to 200° gave 17½ cc. of gas, which contained 15.64 per cent. carbonic acid, 7.71 per cent. oxygen, and 76.65 per cent. nitrogen.

AA. 24 grams of the coke, heated in Reichardt's manner, 15 minutes at 100° gave some 10 cc. of gas, 15 minutes at 150° 8 or 9 cc., and 45 minutes at 200° 12 or 13 cc. In all, the 34 grams of coke heated to 200° gave 33 cc. of gas, which contained 7.71 per cent. carbonic acid and 9.23 per cent. oxygen.

BB. This experiment was tried with some of the coke that was taken directly from a gas retort, but which, after having been powdered, had been left in a corked bottle for two months before it was subjected to examination. It will be noticed that the Sprengel pump was used in this instance, but not in the experiments Y, Z, and AA. 41 grams of the coke were taken. The flask was exhausted before heating it, and then kept at 100° for one hour. 16½ cc. of gas were obtained, which contained 11.86 per cent. carbonic acid, 15.47

per cent. oxygen, 1.10 per cent. carbonic oxide, and 71.57 per cent. nitrogen. On heating for another hour at 200° 19½ cc. of gas were obtained, and this gas contained 29.42 per cent. carbonic acid, 0.36 per cent. oxygen, 1.9 per cent. carbonic oxide, and 68.22 per cent. nitrogen. In all, the 41 grams of coke heated to 200° gave 36 cc. of gas, which contained 21.39 per cent. carbonic acid, 7.27 per cent. oxygen, 1.53 per cent. carbonic oxide, and 69.81 per cent. nitrogen.

For the sake of ready comparison, those results of the two methods of working—viz. with and without the use of the Sprengel pump—which are directly comparable are here given in tabular form:

	Heated to 200° C. At ordinary pressure of air.			Heated to 200° C. In Vacuo.				
SERIES I.—*Air-dried Coke from Dwelling-house.* Per cent. of:	A.	B.	C.	D.	E.	F.	G.	H.
Carbonic Acid	43.03	41.43	42.50	62.97	51.03	62.57	51.46	61.50
Oxygen	...	5.74	6.49	5.31	6.77	2.29	4.06	2.43
Carbonic Oxide	...	...	...	...	3.50	3.69	0.59	...
Nitrogen (by difference)	...	52.83	51.01	31.72	38.70	31.45	43.89	...
		100.00	100.00	100.00	100.00	100.00	100.00	
SERIES II.—*Air-dried Coke from Store-house.*		I.		J.	K.		L.	M.
Carbonic Acid		32.75		61.37	65.42		64.68	74.51
Oxygen		8.21		4.82	0.98		0.41	0.42
Carbonic Oxide		...		...	...		...	1.21
Nitrogen (by difference)		59.04		33.81	...		...	23.86
		100.00		100.00				100.00
SERIES III.—*Old Coke from Out-of-doors.*		N.		O.	P.	Q.	R.	S.
Carbonic Acid		28.31		54.66	52.22	51.22	53.52	60.78
Oxygen		9.02		4.29	2.17	2.16	4.14	1.10
Carbonic Oxide		...		...	...	...	0.39	...
Nitrogen (by difference)		62.67		...	...	...	41.95	...
		100.00					100.00	
SERIES IV.—*Recent, partially-dried Coke.*		T.		U.		V.		W.
Carbonic Acid		32.45		72.45		73.01		75.50
Oxygen		1.81		2.33		1.57		...
Carbonic Oxide		4.00		...		...		...
Nitrogen (by difference)		61.74		...		25.42		...
		100.00				100.00		
SERIES V.—*Coke from the Gas-retort.*	Y.	Z.	AA.			BB. (After standing for two months in a bottle.)		
Carbonic Acid	7.36	15.64	7.71			21.39		
Oxygen	5.10	7.71	9.23			7.27		
Carbonic Oxide	...	...	...			1.53		
Nitrogen (by difference)	87.54	76.65	...			69.81		
	100.00	100.00				100.00		

On examining the foregoing results it will be seen that the gas expelled from the cokes at 100° almost invariably contained a smaller percentage of carbonic acid and a larger proportion of oxygen than were found in the gas obtained by heating to 200°. Compare experiments E, F, G, H, K, M, P, R, S, BB; and the exceptions Q (less oxygen), and W (more carbonic acid). Manifestly the larger amounts of oxygen, and of nitrogen also, that are obtained at the lower temperature must keep down the proportion of carbonic acid in the measuring tube. So too we have always found a comparatively large proportion of nitrogen in those samples of gas which were obtained by working in Reichardt's manner; a fact which is in full accord with our inability to drive off, in this way, from the coke as much of the occluded carbonic acid as was readily removed by means of the Sprengel pump. For the nitrogen obtained by operating by Reichardt's method being less diluted with carbonic acid than that got with the Sprengel pump, must necessarily seem to be predominant. It is not impossible that the large amounts of nitrogen found in so many different solids by Reichardt and Blumtritt[1] in their experiments might have been appreciably lessened if a better chance had been offered for occluded carbonic acid to escape. In any event the experiments of Reichardt and Blumtritt go to show that a part at least of the nitrogen occluded by solids escapes rather easily on heating. The same thing is to be inferred from the observation of Angus Smith,[2] who found that "nitrogen and hydrogen, when absorbed by charcoal, diffuse into the atmosphere of another gas with such force as to depress the mercury three-quarters of an inch." De Saussure[3] found long ago that much of the nitrogen and hydrogen absorbed by dry charcoal is readily discharged again when the coal is immersed in water.

It seems plain at all events that the carbonic acid obtained by either of the methods employed by us must have really been held as such in the cokes at the beginning of the experiments, and that it was not formed during the experiments by the action of entangled oxygen upon the heated carbon, as might perhaps have been inferred from the observations of Angus Smith[4] on the action of oxygen on charcoal, and possibly from those of Varrentrap[5] relating to the oxidation of organic matters at temperatures higher than 100°.

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[1] Journal für praktische Chemie, 1866, **98**, 426 to 479.

[2] Proceedings of Royal Society, 1863, **12**, 425.

[3] Gilbert's Annalen der Physik, 1814, **47**, 122.

[4] *Loc. cit.*

[5] Dingler's Polytechnisches Journal, 1865, **175**, 156, and **178**, 379.

It may here be said that we have seen nothing in the course of our investigations to indicate that there was any appreciable action of oxygen upon the coke at temperatures no higher than 200° during the time actually devoted to an experiment. Reichardt[1] also, for his part, was convinced that no such oxidation need be feared; for he directs that "in cases where the temperature is to be no higher than 200°, a bit of linen may be employed, without harm, instead of a disk of wire-gauze, to hold the powdered substance in the flask." But on the other hand the increase of carbonic acid in that portion of our "coke taken directly from a retort" (Series IV, BB), which had been kept in a bottle during two months, goes to show that slow oxidation of the coke by means of oxygen absorbed from the air may perhaps have occurred in that particular case.[2]

It is noticeable that the amounts of oxygen obtained from the coke are usually sufficient, and in some instances more than sufficient, to account for all of this gas which could possibly have been present in the flask at the beginning of the experiment in the form of entangled air.

A large proportion of the nitrogen recorded in our analyses was doubtless actually expelled from the cokes on heating them. No great amount of it can be justly accredited to the entangled air.

In general, we were unable, either by means of nitrogen or boiled water, or by pumping at the ordinary temperature, to get rid of all the atmospheric air which clung to the coke, though in several instances we reduced the proportion of it very decidedly. It appeared that the gas which came forward on using the pump without heating the coke was practically atmospheric air (compare exps. D and J). On allowing samples of coke to remain in a vacuum from 2 to 4 days, at the ordinary temperature of the air, small quantities of gas were given off which contained more oxygen and less carbonic acid than the gas obtained by heating. In one case the gas obtained in the cold in this way amounted to $\frac{1}{20}$, and in another instance to $\frac{1}{3}$ of the volume subsequently obtained by heating the coke to 200° (compare exps. R and W and X). As a rule, however, it was not until the coke was heated that the last portions of the entangled air passed over into the collecting tube, together with gases actually expelled from the coke. It was in order to do away with this difficulty if possible, and in any event to test the significance of it, that we made the attempts to completely expel the entangled air either by immersing the coke in boiled water, or by subjecting it to a current of pure nitrogen gas, as has been recorded above. Some air was undoubtedly expelled by both these devices, though the influence of the operation on the final results of the experiment was not very great (see for example experiments O, P, Q and R). When water was used to expel the air, more or less trouble was occasioned by its condensing in the Sprengel-pump and in the tubes used for collecting the gas. The pure nitrogen gas served a better purpose than the boiled water, but it still appeared that the air entangled by the coke did not diffuse into this cleansing nitrogen so readily as might have been wished. It should be said that we made no special effort to drive out the last traces of gas from the cokes by long-continued heating at any one particular temperature. It seldom happened, for example, that the temperature of 200° was maintained until gas absolutely ceased to come forward, and we have little doubt that in some instances small additional quantities of gas might have been obtained by longer-continued heating at that temperature. So too in the experiments where tubes containing coke were heated to redness, in connection with the Sprengel-pump, rather more gas could have been got if the tubes had been heated longer at that particular temperature. We intended to push these trials further, and to maintain the highly-heated tubes at special temperatures during definite times similar to those adopted in the foregoing experiments. Such experiments would have been specially interesting in enabling us to compare our work more nearly with that of Parry[1] than we have thus far been able to do. We hope to accomplish this purpose at some future day.

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[1] Fresenius's Zeitschrift, 1868, 7, 186.

[2] For several successive years, in heaps containing a ton or two of coke which had been thoroughly wetted in the process of quenching and then left to dry slowly under cover, I have noticed that after two or three months there are formed, upon some fragments of the coke, mammillated incrustations, often of considerable superficial extent, of crystallized calcite. Both the appearance of these incrustations and the circumstances under which they were formed seemed to show that the carbonic acid as well as the lime had been derived from the coke itself.—F. H. STORER.

Examination of Coke Cinders.—A number of half-burned pieces of coke were picked out from the ashes of a fire which had recently burnt out upon a grate; they were ground to powder and tested in connection with the Sprengel pump. One portion of the material weighing 28 grams was put in a flask, and, after the air had been exhausted, it was heated during one hour at 100° and during another hour at 200°. Five cc. of gas were obtained in all, which contained 4.32 per cent. of carbonic acid and 11.11 per cent. of oxygen. Another portion of the cinders weighing 42 grams, similarly treated, gave 7 cc. of gas, which contained 25.64 per cent. of carbonic acid, 9.96 per cent. of oxygen, and 64.40 per cent. of nitrogen.

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[1] Chemical News, **25**, 98; and, further, American Chemist, **4**, 254.

Examination of Calcined Loam.—Loam from an old pasture was roasted in a muffle, at the lowest possible temperature, until the organic matter was completely destroyed, and the product was subjected to experiment. 27 grams of the calcined earth were placed in a flask, the air was exhausted, and a 14 cc. sample of the outcoming air was collected for analysis. It was found to contain 0.36 per cent. of carbonic acid and 19.67 per cent. of oxygen. The earth was then heated for one hour at 100° and for another hour at 200°, but the amount of gas obtained was too small to measure; yet when another 25-gram portion of the earth was heated during two hours at 200°, after the air had first been pumped out of the flask, it gave 12 cc. of gas which contained 5.84 per cent. of carbonic acid, 15.43 per cent. of oxygen, and 78.73 per cent. of nitrogen. Curiously enough, another 67-gram portion of the earth behaved like the first. After the air had been exhausted from the flask the latter was heated one hour at 200°, then allowed to stand a day and a half, and again heated during three hours at 200°. But the amount of gas obtained was too small to measure and analyze. On the other hand, a measurable quantity of gas was obtained from a 31-gram portion of the earth heated two hours at 200°, but this gas was accidentally lost. As was the case with the coke cinders mentioned above, we think it probable that these differing results may depend upon a lack of homogeneity in the material operated upon. In yet another trial 90 grams of the calcined loam were placed in a flask, the air was exhausted, and the apparatus allowed to stand with the earth *in vacuo* for four days. On then heating two hours at 200°, 6 cc. of gas were obtained which contained 25.84 per cent. of carbonic acid, 10.76 per cent. of oxygen and 63.40 per cent. of nitrogen. The results of this trial are manifestly more trustworthy than those of the preceding tests. It may be remarked in this connection that we had already, several years ago, proved qualitatively the presence of carbonic acid in calcined loam such as this now under consideration (see Bulletin of the Bussey Institution, **2**, 204). Finally, another 28-gram portion of the calcined loam was placed in a tube of hard glass, the air was exhausted, and the tube heated to low redness for an hour; 7 cc. of gas were obtained which contained 72.74 per cent. of carbonic acid and 6.46 per cent. of oxygen. The proportion of oxygen is noticeably large in all three of the experiments upon calcined earth; and so it was in the case of the coke-cinders also. The latter were of course admixed with more or less ashes that adhered to them. We have to thank our assistant, Mr. D. T. Hinckley, B. A. S., for efficient aid in this investigation.

Laboratory of the Boston Gas Light Co.

DETERMINATION OF ORGANIC MATTER IN POTABLE WATER.[1]

Second Paper.

By Prof. J. W. Mallet, F. R. S.
University of Virginia.

Origin and Character of the Research.

At the close of the report on the extended investigation of the chemical methods heretofore in use for determining organic matter in potable water,[2] certain suggestions were made as to possible improvements in these methods, tending to remedy defects which had been discovered in the course of the research. By direction of the Executive Committee of the National Board of Health, given during the past summer, the most important of these suggested improvements have been practically studied, and the results are now reported upon.

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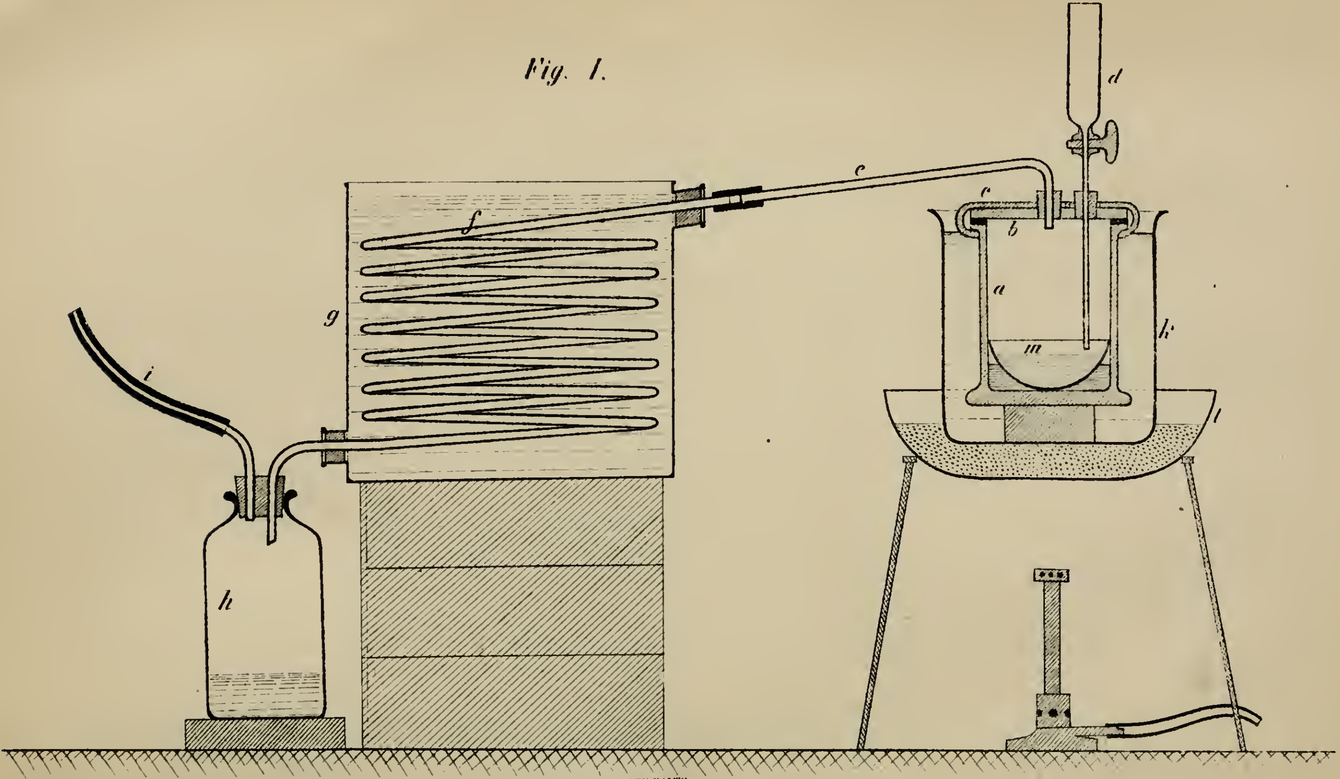
[1] Report on the results of a supplementary investigation, made by the direction of the National Board of Health.

[2] See this Journal, **4**, 241 and 334, and Supplement No. 19 of the National Board of Health Bulletin, May 27, 1882.

Fig. 1.



I FRIEDENWALD, LITH BALTO.

COMBUSTION PROCESS.

1. *Evaporation of the water under much diminished pressure, in a vessel excluding contact with the atmosphere.*

The apparatus employed for this purpose was arranged as shown in Fig. 1.

The vacuum vessel (*a*) was a tolerably stout glass jar, such as anatomical preparations are kept in, the mouth of which had been ground flat upon a plane surface, and was covered by a disk of thick plate-glass (*b*), with two bluntly tapering holes drilled through it. A strip of thick, hard sheet brass (*c*), having two holes in it corresponding to those in the glass disk, served to form a clamp by which this disk was firmly pressed down upon a ring of sheet India-rubber laid as a washer on the ground mouth of the jar. The holes were fitted with good, soft India-rubber stoppers, through one of which passed a funnel (*d*), with well ground glass stopcock, and tube of almost capillary bore, while through the other passed the glass tube (*e*), serving to carry off the vapor as formed, which tube was connected with the block-tin worm (*f*), surrounded by ice-water in the worm-tub (*g*), and delivered water as condensed into the stout bottle (*h*), from which the thick India-rubber tube (*i*) led to the jet-pump serving to produce exhaustion. The vacuum vessel (*a*) was supported above the bottom of a large glass beaker (*k*) serving as a water-bath, and this in turn was supported on a sand-bath (*l*) above a Bunsen gasburner with "rose" top.

The specimen of water to be examined was evaporated in a glass dish (*m*) of about 4 inches in diameter, placed at the bottom of the vacuum vessel. At first this dish was supported in an upright position by a brass ring, and only touched the glass of the outer vessel at one point at bottom, but it was soon found that with this arrangement the transmission of heat from the water-bath was quite too slow, and hence some mercury was placed in the bottom of (*a*), and the dish was immersed in this to a considerable part of its depth. The jar (*a*) was about 6 inches deep, and of a diameter just sufficient to allow the glass dish to drop down easily, but I should prefer to diminish the depth, and would indeed rather use a simple glass dish, of stout glass, with turned-over lip ground to receive directly the India-rubber washer and plate-glass cover, thus dispensing with the separate vacuum chamber altogether, and leaving but a single thickness of glass between the water-bath and the water to be evaporated. As my apparatus was arranged, no inconvenience was experienced from vapor of mercury, but in long continued use no doubt enough of this vapor would be given off under the reduced pressure to attack the block-tin worm and make it brittle.

Owing to the slow transmission of heat at the comparatively low temperature employed, the water-bath had to be considerably warmer than the water in the dish within. The bath had immersed in it a thermometer, and was kept filled to the proper height by a constant-level feed, not shown in the figure. The worm-tub was filled with water at the outset, and afterwards fed with lumps of ice; an overflow tube, also not shown in the figure, served to carry off surplus water. If the apparatus were left at work during the night it would become necessary to supply ice-water to the condenser from a large reservoir by a constant-level feed-pipe.

It is desirable that the tubes, both of glass and of block-tin, through which the escaping vapor passes, should have an interior diameter of not less than a third of an inch.

In my experiments the water to be evaporated was introduced, about 50 cc. at a time, by pouring into the wide portion of the funnel (*d*) and very cautiously opening the stopcock. This funnel might, however, be replaced by an almost capillary tube with a glass stopcock upon it, connecting the vacuum chamber with the bottom of a flask containing the whole quantity of water to be evaporated, this flask being placed out of the reach of the heat from the lamp and water-bath; after the temperature and pressure within the apparatus have become approximately constant the stopcock might be set very partially open, so as to allow of continuous supply of more water at just the rate demanded by the progress of the evaporation. In any case the vacuum must be gradually and cautiously established at first, in order to avoid any spattering of the contents of the dish from the escape of bubbles of dissolved gases, and for the same reason each new portion of water must be introduced cautiously, not too much at a time. The stopcock on the inlet tube must be thoroughly well ground, so as to work and remain tight without any lubricant.

The vertical limb of the exit tube for the vapor should be as short as possible, to prevent any risk of liquid water condensing in it and dropping back into the dish, thus producing splashing, and with the same object in view this short vertical portion of the tube and the whole of the top of the glass covering plate are with advantage to be protected from cooling by some loose cotton-wool. The longer limb of the same exit tube should have a decided downward inclination, so as to prevent any condensed water running back.

Using mercury in the bottom of the vacuum chamber, it was heavy enough to rest steadily on its support, but if this were not the case, and there were a tendency to float up, a simple clamp could of course be used to hold the vessel firmly down.

During the greater part of my work the barometer was at something like 745 mm., and the mercury in the jet-pump gauge stood at about 690–700 mm. Entire freedom from any return of air or water through the pump, and from any abrupt oscillations of the gauge, was secured by an oiled-silk valve, opening only towards the pump, which was inserted in the line of tubing connecting the latter with the evaporation apparatus.

The temperature of the water-bath was so regulated as to keep the water in the glass dish very near, but distinctly below its boiling point for this reduced pressure. The water was therefore evaporated at but little over 30° C., though the thermometer in the water-bath was at 55° or 60°. Of course actual boiling must not be permitted, as it would almost certainly lead to loss of water from the dish.

It was found possible to complete the evaporation of half a litre of water in this apparatus between daylight and dark on a long summer day—say within fifteen hours; but of course the rate of evaporation will depend much upon the more or less free consumption of water in running the jet-pump, so as to steadily maintain a high degree of exhaustion, and the same amount of water may be treated in less time if with higher pressure a higher temperature be permitted.

In order to test the advantage supposed to be obtainable from this method of evaporating water for the combustion process, organic matter had to be introduced in accurately known quantity, and for this purpose leucine and tyrosine were selected, as representing the more stable products of putrefaction liable to occur in natural water, and for which nevertheless the combustion process in its usual form had been found to give results far from satisfactory. Eight experiments were made with each of these substances, using from 5 to 40 milligrammes per litre of water. The results of the sixteen combustions were as follows:

TABLE I.

	Amount obtained, as percentage on amount originally present.		
	Greatest.	Least.	Average.
Leucine.			
Carbon . . .	97.24	91.40	95.77
Nitrogen . .	95.64	88.27	93.32
Tyrosine.			
Carbon . . .	98.13	92.65	97.04
Nitrogen . .	97.29	90.45	95.72

These figures show a marked improvement upon the results obtained with the same substances by Mr. Noyes, using the Frankland process in its usual form. There is a much nearer approach to the recovery of the quantities of carbon and nitrogen really present in the water as taken for analysis. The two elements are recovered in much more nearly the true proportion to each other. The error for each is in the same direction, that of partial loss, instead of there being a large *excess* of nitrogen. We may fairly conclude therefore that there is real advantage in evaporating the water at the low temperature made available by diminished pressure, and with exclusion of atmospheric air.

It is to be observed, however, that there is uniformly *some* loss, although to a comparatively small extent, so that even for analyses made under these favorable conditions it cannot be rightly claimed that the results represent the whole of the organic matter originally contained in the water. Moreover, it is probable that much of the organic matter occurring in natural waters, and it is certain that some of it, is of less stable character than the leucine and tyrosine experimented on, and for such less stable material larger losses may be expected.[1] And, furthermore, Frankland has found that simple evaporation with sulphurous acid, even at a temperature near 100° C., will not suffice to entirely decompose the carbonates of a natural water, but that active boiling of the water for at least a few seconds after the addition of sulphurous

[1] It has been found by Dietzell (Berichte d. deutsch. chem. Gesellsch. **15**, 551) that during putrefaction very considerable quantities of free nitrogen may be evolved by the formation of nitrous acid and its reaction on leucine, primary amines and ammonia.

acid is necessary;[1] some injury to the organic matter may be done by such high temperature applied even for so short a time, though the mischief will probably be small. In the experiments just recorded, sulphurous acid, to the extent of about a third of the usual quantity, was added, but the water was not boiled, there being no carbonates present.

Evaporation of the water with magnesia, in order to remove ammonia existing as such or as ammoniacal salts.

Lechartier has advocated[2] the removal of ammonia by evaporation with magnesia, the determination, in the residue, of the nitrogen of organic matter and nitrates, a separate determination of the nitrates, and calculation of the organic nitrogen by difference. It was proposed in my general report to modify this plan by evaporating with magnesia so as to get rid of ammonia, reducing nitrates in the residue brought to a small volume, but not to dryness—as directed by Frankland, by addition of sulphurous acid with a drop of a solution of a ferrous salt and evaporation to dryness, and finally determining organic nitrogen only in the dry residue by combustion.

In investigating this use of magnesia, however, a difficulty was encountered which vitiates Lechartier's method as well as my proposed modification of it. He says that evaporation with magnesia at the temperature of the water-bath, while it completely expels ammonia, does not decompose organic substances, such as urea, and gives in proof of this assertion the results of some experiments, in all of which urea was the only organic substance present. This statement I am unable to verify. I have tried several forms of nitrogenous organic matter liable to occur among the products of putrefaction, and have found that at temperatures no higher than 40° to 50° C. magnesia in the presence of water slowly attacks them, evolving small amounts of ammonia, detectable by litmus paper and paper moistened with the Nessler test solution.

The magnesia was prepared by careful ignition of pure magnesium carbonate, and was very carefully washed to free it from any possible trace of alkali. It was placed, with a few cubic centimetres of water and the organic substance to be experimented on, at the bottom of a short, wide test-tube, the mouth of which was closed by a cork, serving to suspend a strip of the moistened test-paper, and the lower part of the tube was then immersed in a water-bath kept at the required temperature.

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[1] It might be worth trying whether the decomposition of carbonates could not be advantageously accomplished by some of the acid salts, such as the acid phosphate of calcium, magnesium or sodium.

[2] Comptes rendus, **89**, 231. Ann. de Chim. et de Phys. [V], **19**, 257.

Salts of the amines on being thus treated very naturally affected the test-paper at once, and even at common temperature.

Specimens of urea, both of natural and artificial origin, recently recrystallized, gave the reactions of ammonia distinctly and in a very short time at 40° to 45° C. It is stated that the amic acids are not decomposed with evolution of ammonia even by boiling with solutions of the alkalies, but leucine treated as above described with magnesia at 50° C. gave the reactions of ammonia distinctly, though somewhat slowly. Tyrosine behaved in the same way; it seemed to be rather more stable.

Benzamide apparently resisted decomposition, at any rate for some minutes, at 55°, but signs of the ammonia reactions began to appear at 100°.

Hence it appears that magnesia cannot be relied upon to expel pre-existent ammonia only from an evaporated water, leaving nitrogenous organic substances untouched. The long-continued contact with the water as its dissolved contents become concentrated, even at the low temperature made available by lowering of pressure, must produce losses of organic nitrogen, which may very possibly be accompanied by loss of carbon from the same constituents.

It may, however, perhaps be the case that in waters containing relatively very large quantities of ammoniacal salts, the error due to the cause under notice would be less than that attributable to the dissociation of these salts, to an extent not accurately determinable, during the evaporation.

Reduction and removal of nitrates by evaporation of the water with hypophosphorous acid.

In the main report on this water-analysis investigation it was stated that some preliminary experiments made by myself had seemed to show that nitrates and nitrites may be completely reduced by evaporating to a small bulk with no great excess of phosphorous or hypophosphorous acid, guarding against the evolution of phosphuretted hydrogen by the low temperature employed, then adding magnesia in small excess and completing the evaporation, thus leaving the residue in a pulverulent instead of a sticky condition, easy of removal from the dish, and probably allowing of complete combustion without inconvenience from the final oxidation of the small excess of phosphite or hypophosphite, and without any wrapping up of carbon particles. It was suggested that this plan was deserving of being tested.

It has now been tested, and with satisfactory results so far as the experiments have gone. Solutions of tyrosine, 20 parts per million of water, to which 10 parts of nitrogen per million had been added in the form of potassium nitrate (72.2 parts of this salt), were evaporated with 2 to 5 cc. of a moderately strong solution of hypophosphorous acid. The highly concentrated, but not yet dry, residues were carefully tested for the nitrate by means of brucine, and for nitrite by Griess' naphthylamine reaction, but negative results were obtained as to both. There was no darkening, or other apparent indication of the tyrosine being attacked, and on adding magnesia in excess, as proposed, to residues from the evaporation of similarly treated solutions and completing the drying, the combustion in the Sprengel vacuum was carried out without any special difficulty. In a natural water the carbonates present would be decomposed by the hypophosphorous acid, and carbon dioxide would be expelled during the evaporation.

In applying this method, using magnesia to neutralize the excess of acid and to dry up the residue to a condition in which it can easily be removed from the dish and mixed with cupric oxide, care must of course be taken that the magnesia is thoroughly ignited before being used, that it is not exposed to any considerable extent to the air after it has been so prepared, that the evaporation is carried on in such a vacuum chamber as has been described, and that the dried residue is not for any needless length of time exposed to the atmosphere before introduction into the combustion tube. Neglect of these precautions would lead to absorption of carbon dioxide, and consequent vitiation of the results as far as carbon is concerned. To avoid, however, the difficulty which had been ascertained to exist, arising from the action of magnesia on nitrogenous organic matter, it was thought best to use barely enough magnesia to neutralize the excess of acid, and to complete the drying up with an addition of pure *silica*, prepared by ignition of silicic acid, itself made from silicon fluoride. With this modification of the plan proposed the combustion gave results for the carbon and nitrogen of the tyrosine as good as those obtained on the average from the solutions of this substance in pure water without additions.

The solution of hypophosphorous acid should be carefully guarded from the air, and its strength ascertained from time to time (in order to judge approximately of the quantity to be used), not by neutralization, but by the reducing action upon a solution of mercuric chloride.

ALBUMINOID-AMMONIA PROCESS.

The examination of modified forms of this process was undertaken by Dr. Charles Smart, U. S. A., who has furnished the following statement of results obtained. The appointment of Dr. Smart to the office of Secretary to the National Board of Health, and the pressure of duties thus entailed upon him, have prevented the whole plan of experiments intended being carried out, but the main points on which information was sought have been covered.

"The experiments detailed below were intended to determine the conditions under which ammonia in small quantities is evolved from its containing liquid, and those under which perfect condensation or absorption may be subsequently obtained.

Series of Experiments on the Liberation and Condensation of minute quantities of NH_3.

The charge for distillation consisted of so many cc. standard NH_3 solution (1 cc. = .01 mgrm. NH_3) + so many of ammonia free water, making a total of 500 cc.

A. 1 mgrm. NH_3, ordinary distillation. Temperature of distillate 27° C.

.50 .21 .055 .01 = .855 = 14.5 per cent. loss.

Compare with H and I.

B_1. .5 mgrm. NH_3, ordinary distillation. Temperature of distillate 28° C. Temperature in retort 101° C.

.40 .06 .005 = .465 = 7 per cent. loss.

B_2. 1 mgrm. NH_3. Conditions as in B_1.

.76 .10 .01 .00 = .87 = 13 per cent. loss.

Compare with A in which gas-jet was smaller and time of distillation longer.

B_3. 2 mgrms. NH_3.

1.34 .32 .05 .015 .00 = 1.725 = 13.75 per cent. loss.

C_1. 1 mgrm. NH_3, receiver closed by sulphuric acid bulbs, connected with water-jet, tension reduced six inches; retort heated in vessel of boiling water. Temperature in retort 95° C., of distillate 28° C. Distillation slow (90 minutes for 50 cc).

.46 .28 .14 .035 .015 with .01 in acid = .94 = a loss of 6 per cent.

C_2. 2 mgrms. NH_3. Temperature in retort 96° C.; other conditions as in C_1.

.77 .56 .27 .12 .06 .025 with .035 in acid = 1.84 = a loss of 8 per cent.

D_1. .5 mgrm. NH_3. Conditions as in C, but flame applied to retort. Temperature in retort 97–97.5° C., of distillate 28° C. Distillation rapid (12 minutes for 50 cc).

.36 .075 .01 with .02 in acid = .465 = a loss of 7 per cent.

D_2. 1 mgrm. NH_3.

.72 .20 .035 .015 with trace in acid = .97 = a loss of 3 per cent.

D_3. 2 mgrms. NH_3.

1.41 .36 .05 .01 and trace only in acid = 1.83 = a loss of 8.5 per cent.

E_1. .5 mgrm. NH_3, ordinary distillation, but receiver closed by sulphuric acid bulbs. Temperatures 101° and 28° C.

.37 .075 .015 with .02 in acid = .48 = a loss of 4 per cent.

E_2. 1 mgrm. NH_3.

.72 .19 .035 .005 with .02 in acid = .97 = a loss of 3 per cent.

E_3. 2 mgrms. NH_3.

1.39 .34 .07 .01 with .03 in acid = 1.84 = a loss of 8 per cent.

Compare E with B_1.

F_1. 1.5 mgrm. NH_3. Conditions as in E, but pure water in bulbs instead of sulphuric acid.

1.12 .20 .02 .005 = 1.345 = 10.3 per cent. loss.

G_1. .5 mgrm. NH_3. Conditions as in F, but with water-flask as guard beyond the water-bulbs.

.37 .07 .015 = .455 = a loss of 9 per cent.

G_2. 1 mgrm. NH_3.

.72 .18 .03 .0025 and trace in bulb = .9325 = 6.75 per cent. of loss.

G_3. 2 mgrms. NH_3.

1.41 .32 .065 .01 with trace in water = 1.805 = a loss of 9.75 per cent.

Compare G with E and B.

H_1. .5 mgrm., ordinary distillation. Temperature of distillate 6° C.

.40 .08 .02 .00 = .50

H_2. 1 mgrm. as in last.

.80 .14 .03 = .97 = loss of 3 per cent.

H_3. 1 mgrm. as in last.

.80 .15 .03 = .98 = loss of 2 per cent.

I_1. .5 mgrm. condensed in coil 18 feet long. Temperature of distillate 6° C.

.08 .32 .08 .015 .005 = .50

I_2. 1 mgrm. as last.

.43 .38 .12 .04 .01 = .98 mgrm. = loss of 2 per cent.

I_3. 1 mgrm. as last.

.35 .40 .12 .07 .03 = .97 mgrm. NH_3 = loss of 3 per cent.

Second Series of Experiments on the Liberation and Condensation of minute quantities of NH_3 *from Water.*

I. .5 mgrm. NH_3, in a retort connected with a water-jet pump, no condenser, but sulphuric acid bulbs between retort and pump, 6¾ inches pressure removed; stream of air passing through apparatus entering by means of a glass wool filter moistened with sulphuric acid. Temperature 28° C. After 24 hours .11 mgrm. NH_3 was found to have left the retort for the acid bulbs.

II. .5 mgrm. NH_3, apparatus as in I, but temperature in retort kept at 63° C. At end of 21 hours, 190 cc. of the water were found to have passed into the acid bulbs and flasks carrying with them all of the NH_3.

III. .5 mgrm. NH_3, apparatus as last. Temperature in retort 55° C. At end of 18 hours, 85 cc. were found to have passed over carrying with them .488 mgrm. NH_3.

IV. As last. At end of 6 hours, 31 cc. had passed over with .29 mgrm. NH_3.

V. As last, but with the air drawn *through* the liquid to cause an artificial ebullition. At the end of 5 hours, .27 mgrm. was found in the acid.

VI. As last, but with 9 inches pressure removed. Temperature 50° C. At the end of 16 hours, 60 cc. had come over bringing all the NH_3.

VII. As last. At end of 4 hours the 10 cc. which had come over contained only .25 mgrm. NH_3.

VIII. As last, but with 10½ inches pressure removed. Temperature 49° C., and 6½ hours of exposure, 13 cc. passed over containing .27 mgrm. NH_3.

Experiments on the Decomposition of Urea during Distillation of the Water holding it in solution.

The urea used in these experiments contained .45 per cent. of free NH_3. This amount must be deducted from the first recorded results of every experiment.

1st. 10 mgrms. urea (containing .045 mgrm. NH_3) in 500 cc. water distilled from water-bath, and with 6½ inches pressure removed from interior of apparatus. Temperature in retort 96° C. Two hours required for the distillation of each measure of 50 cc.

Result 1st measure .19 mgrm.
2d " .37 "

2d. 10 mgrms. urea, but without the water-bath and jet-pump. Distillation rapid. 12 minutes for 50 cc.

1st measure .12 mgrm.
2d " .10 "

3d. 20 mgrms. (containing .09 mgrm. NH_3) operated on as in experiments I, II, III, &c. At end of 5 hours, 40 cc. had passed over carrying with them .19 mgrm. NH_3 into the acid.

4th. 20 mgrms. urea were permitted to remain under the influence of the jet-pump and passing air current as in I for 40 hours; .14 mgrm. was found in the acid.

5th. 20 mgrms. were exposed in solution to the air for 40 hours, and at the end of that time showed the presence of .09 mgrm. NH_3 as when freshly dissolved.

6th. 20 mgrms. at 60° C. and 6½ inches for 7 hours gave .20 mgrm. NH_3 in 40 cc. which passed over into the acid bulbs.

7th. 20 mgrms. at 60° C. and 6½ inches for 16 hours gave in 65 cc. distilled .25 mgrm. = .16 mgrm. when the .09 free NH_3 is deducted.

8th. 35 mgrms. urea (containing .16 mgrm. NH_3) at 55° C. and pressure as in last gave after 16 hours 67 cc. containing .29 mgrm. NH_3.

9th. 35 mgrms. urea as in last, but with only 6 hours exposure, gave .035 mgrm. in 26 cc. distilled. This .035 represents the decomposition effected during the time, as the residue from 8 was used and it was free from the original ammonia taint of the urea.

10th. The residue from 9 treated as before for 16 hours gave .09 in the 70 cc. which passed over.

A comparison of C and D shows that water containing a trace of ammonia may be heated within a degree or two of its boiling point without any rapid evolution of the ammonia, but that as soon as the extra degree or two needful to cause ebullition has been added, the ammonia passes over rapidly with the watery vapor. Ninety minutes of a heat just below the boiling point are required to accomplish what may be effected in twelve minutes if that point is attained. A reduction of pressure on the surface of the liquid promotes the evolution, by causing ebullition at a lower temperature; compare D with E. A diminished pressure no doubt acts at all temperatures in aiding the evolution; and a weak solution as in I may lose its ammonia at ordinary temperatures, but the length of time required to effect this renders the process valueless as a practical method. Nevertheless, by increasing the temperature under the lessened pressure the time required may be so reduced as to give the process a value in practice.

As the rapidity of the evolution of the ammonia from the water containing it depends mainly on the presence of heat sufficient to boil the water, so a perfect condensation, where heat has been applied to cause rapid evolution, can only be obtained by the needful reduction of temperature; compare the whole series A, B and C with H and I. Where the condensing liquid runs freely from the tap through the condenser so as to give the distillate a temperature a few degrees above the freezing point, the ordinary condenser is as efficient as one with a condensing tube many times longer; compare H and I.

But where the liberation of the ammonia is effected slowly under reduced pressure and at temperatures considerably below the boiling point, the whole may be recovered by absorption in acid without the aid of a condensing circulation. See experiments II, III, and VI.

As with the evolution of ammonia, so with the decomposition of urea: it is effected slowly at temperatures below the boiling point, but as soon as that point is reached the ammonia from its dissolution is given up rapidly. Compare experiment 2 with the others of that series.

Practically it may be said that where we are dealing with free ammonia and non-volatile and stable organic matter in a water, the ordinary process with a condensing medium which gives a proper temperature to the distillate may be considered satisfactory.

But where we have to discriminate between free ammonia and urea, the slower method by absorption in acid under reduced pressure may be of value. The experiments 3–8 show that if the operation is commenced in the afternoon and permitted to continue until next morning, the whole of the ammonia may be expected in the acid bulbs, and this may be assumed with greater certainty if more than one-tenth of the liquid has distilled in the meantime; but if the operation is commenced in the morning or forenoon, it is doubtful if it can be completed in the ordinary working hours of the laboratory. Experiments 7–10 indicate that during this liberation of the free ammonia present, the urea which may accompany it will only suffer decomposition to the extent of from three to eight tenths of one per cent.

CH. SMART, *U. S. Army.*"

PERMANGANATE PROCESS.

Maintenance of an approximately constant excess of permanganate during the progress of action on the organic matter in a sample of water.

The effect of thus modifying the permanganate process as described and used by Tidy was tested as follows: The process was first applied in its usual form to water artificially polluted with organic matter,[1] extending, however, the time of action to 24 hours, and making determinations in separate flasks of the oxygen consumed at the end of 1, 3, 6, 9, 12 and 24 hours respectively. Enough of the organic matter was used to consume altogether a large proportion of the oxygen of the charge of permanganate. Having plotted off a curve on paper representing the rate of consumption of the oxygen as thus found, it was determined how much additional permanganate should be added at the end of each half-hour for the first three hours, at the end of each hour for the succeeding nine hours, and at the end of each six hours for the remaining twelve hours, in order to maintain as nearly as these intervals would permit, a constant excess throughout the whole period. These additions were made at the proper times to a new lot of the polluted water altered only by keeping for one day, and determinations were made as before of the oxygen consumed at the end of 1, 3, 6, 9, 12 and 24 hours.

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[1] An infusion of dead forest leaves and the drainings from a pile of animal manure were the polluting materials used.

Results a little higher were obtained by this modified process as compared with those given by the former method. The difference, however, was not very great. The chief evidence of greater regularity of action was furnished by experiments, made simultaneously, on two different dilutions of the same solution of organic matter. These gave results as to oxygen consumed which were almost exactly in proportion to the difference of strength when the modified process was used, whereas the stronger solutions gave somewhat lower results than would have been calculated from those for the weaker dilutions when the original form of the process was applied. These comparative experiments were too few in number to generalize from with much positiveness, but they may fairly be taken, as far as they have gone, in confirmation of the soundness of the principle on which the suggested improvement is based.

ON THE ACTION OF CERTAIN VEGETABLE ACIDS ON LEAD AND TIN.

By Francis P. Hall.

The enormous and continually increasing use of canned goods—fruit, vegetables, meat, etc.—has led to the discussion, on sanitary grounds, of the possible injurious effect of the material of the can on its contents; and, among other chemical questions, is that of the effect of various vegetable acids upon the material of the cans, *i. e.* upon the can itself and upon the solder which may be exposed on the inside. The fear also has arisen lest the tin-plate itself of which the cans are made should, for the sake of greater cheapness, be made not with pure tin, but with an alloy of lead and tin.

The following paper contains the results of experiments on the action of certain acids on tin and on alloys of tin and lead, and also the results of some investigations as to the quality of the tin-plate and tin-foil in actual use as envelopes for food products.

On the Action of Vegetable Acids on Alloys of Lead and Tin.

One of the most important things to be considered in investigating the power of an alloy to resist corrosion is the electrical relation of the metals which compose it. Lead and tin are so nearly alike in this respect that their relation to each other may be reversed in different liquids, or even in the same liquid under different circumstances. On this subject chemical literature contains many and quite discordant statements. It seems, however, to be fully established by the experiments of Weber[1] that ordinary vinegar will dissolve lead from an alloy of lead and tin containing only 5 per cent. of lead, and further, that from a dilute acidulated solution of acetate of lead, lead is precipitated by an alloy containing as little as 5 per cent. of tin.

In the following investigation I wished to ascertain quantitatively the action of several of the more common vegetable acids, all quantitative experiments that I had seen being made with acetic acid only.

To ascertain definitely the effect of alloying on the corrosion of the metals, the amount of lead or tin dissolved when pure must be compared with the amount dissolved, under the same conditions, from an alloy exposing the same surface of the metals in question. To make the experiment, as is usually done, with equal-sized pieces of pure metal and alloy is not fair, if we consider the action to be proportional to the surface of metal exposed, because then the united surface of the two pieces of pure metal is twice that of the alloy and the surface of either metal exposed in the alloy is less than that exposed by the piece of pure metal.

To overcome this difficulty I proposed to proportion the size of the pure metal plates according to the composition of the alloy. In order to proportion them more easily and to have them of a size readily comparable with one another, I took into account the specific gravity of the metals in making the alloys. Hence, barring the unequal contraction of the metals on alloying, I had alloys exposing a known surface of lead and tin. I could now expose an equal surface of pure metal to the same acid under the same conditions and compare the action, thus getting a fair idea of the effect of alloying the metals, as well as the action of the acid on a known surface of pure lead or tin.

I made after this plan three alloys—one with equal parts of lead and tin, one with an excess of lead, and one with an excess of tin. These were all that I had time to experiment with, but the researches of Weber[1] show that, for acetic acid at least, the action on the alloys increases quite regularly as the proportion of lead increases, therefore the action on alloys containing lead and tin in different proportions than those I took can be inferred with fair accuracy by interpolation.

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[1] Dingl. pol. Jour. 232, 153, 264; Wagner Jahresb. 1879, 196–207.

The alloys were made from pure lead and tin, well stirred when melted, then cast in thin sheets in iron moulds. Afterwards these sheets were rolled into thin strips and trimmed to the size desired. Strips of pure lead and tin were made at the same time. The tin used was Banca tin, containing 99.78 per cent. of tin, a trace of lead and a trace of copper.

For acids I used a solution of glacial acetic acid in distilled water, which, on titration with a standard solution of ammonia, proved to have a strength equal to 5.75 per cent. of acetic acid; also solutions of crystallized tartaric and citric acids, which neutralized the same amount of ammonia.

The tartaric and citric acids contained, as they always do, a trace of lead, but the amount was much too small to appreciably influence the results.

Strips of the alloys 1.2 inch wide and 12 inches long were cut out, exposing, therefore, counting both sides, 28.8 square inches or one-fifth of a square foot. Pieces of pure lead and tin were taken of the same width, but varying in length to suit the composition of the alloy to which each corresponded. These strips of metal were rubbed until perfectly bright, washed with a little dilute alcohol, heated in a drying closet, and when cool weighed. Immediately after weighing they were put into separate beakers each containing 200 cc. of acid. The long strips were coiled and kept off the bottom of the beaker by a V of glass rod. In each case the liquid covered the metal by more than an inch, so that the air did not take part directly in the action. Each beaker was covered with a watch-glass.

After standing for two weeks in a place where the temperature varied from 25° to 35° Centigrade, the contents of the several beakers were examined. The most notable change was that the acid containing the tin, as well as that containing the alloys, had a decided yellowish tint, while that containing the lead was perfectly clear and colorless. The metal in all cases was more or less tar-

[1] *Loc. cit.*

nished, but the tin much more noticeably so than the lead. Two of the alloys in the acetic acid were sprinkled with little black crystals. These crystals were evidently metallic; they were carefully collected, washed with alcohol, dried and analyzed. The result of the analysis is given later. The smallest of the pieces of lead in the tartaric acid was covered with small transparent crystals; these were set aside for further examination. The pieces of tin were covered with a dusty powder, but there was not enough of it to analyze.

When the contents of each beaker had been carefully examined, the strips of metal were lifted out, washed with a jet of water, dried with a soft towel, and, after remaining a while in a drying-closet, weighed. The loss of weight served as a rough check on the subsequent analysis of the solutions. Next, the metal in solution was precipitated by sulphuretted hydrogen. The lead caused dense black precipitates, much finer in the tartaric and citric acid than in the acetic. The tin in the acetic acid came down of a dark brown color, showing the stannous salt, while that in the tartaric acid gave, at first, merely a yellow coloration. After standing some time, however, a flocculent, apparently hydrated precipitate settled out. The same seemed to be the case with the citric acid solutions, but on closer examination an almost transparent precipitate could be seen, and it settled much quicker than in the case of the tartaric acid. These same peculiarities of the precipitates of sulphide of tin were noticed throughout the whole investigation. It was also invariably the case with the alloys that the precipitates in acetic acid were dark brown, while those in tartaric and citric acids were light-colored and flocculent.

After some experimenting I found the best way to separate the sulphides of lead and tin in the solutions was to carefully decant as much as possible of the liquid through a filter, neutralize what remained with ammonia water, add a little yellow ammonium sulphide, and heat; then collect the sulphide of lead on the filter used before. The tin was determined in the alkaline filtrate. The sulphide of lead was converted into the sulphate before weighing; the sulphide of tin into the oxide in the usual manner. In no case was either metal determined by difference.

The results obtained are given in the following tables. The first two columns of Table I give the amount of surface of each metal exposed both as pure metal and in the alloy.[1] The last two give the total weight of metal, lead and tin, dissolved from the alloy, and from an equal surface of the same metals exposed in the pure state. But although the surface exposed was the same, the unalloyed metals were exposed to twice as much acid, each being in a separate beaker with 200 cc. of the acid. This might have been righted by proportioning the acid to the surface exposed, but this did not occur to me until too late. It will be noticed how often the amount dissolved when unalloyed is equal to twice that dissolved from the alloy.

TABLE I.

Kind of Acid.	Surface exposed, in sq. inches.		Percentage composition.		Loss of weight, in grams.	Found in solution, in grams.		Percentage of dissolved metals.		Total amount dissolved (in grams) from	
	Lead	Tin.	Lead.	Tin.		Lead.	Tin.	Lead.	Tin.	Alloys.	Pure Metals.
Acetic ...	7.2	...	100.	...	0.4320	0.4216	...	...	...	...	...
" ...	7.2	21.6	34.1	65.9	0.4525	0.0432	0.3312	11.54	88.46	0.3744	0.7122
" ...	...	21.6	...	100.	...	...	0.2906	...	...	...	...
" ...	14.4	...	100.	...	0.5470	0.5444	...	...	...	...	...
" ...	14.4	14.4	60.8	39.2	0.5145	0.0558	0.3552	13.57	86.42	0.4110	0.8242
" ...	...	14.4	...	100.	0.2820	...	0.2798	...	...	...	...
" ...	21.6	...	100.	...	0.6195	0.6137	...	...	..	...	...
" ...	21.6	7.2	80.84	19.16	0.6570	0.4887	0.1589	75.46	24.54	0.6476	0.8073
" ...	...	7.2	...	100.	0.2135	...	0.1936	...	...	...	...
Tartaric.	7.2	...	100.	...	...	0.0452	...	...	...	...	...
"	7.2	21.6	34.1	65.9	0.0280	0.0029	0.0269	9.73	90.27	0.0298	0.0664
"	...	21.6	...	100.	0.0210	...	0.0212	...	...	...	...
"	14.4	...	100.	...	0.6605	0.0586	...	...	...	...	...
"	14.4	14.4	60.8	39.2	0.0385	0.0042	0.0332	11.23	88.77	0.0374	0.0750
"	...	14.4	...	100.	0.0150	...	0.0164	...	...	...	...
"	21.6	...	100.	...	0.0655	0.0654	...	...	...	...	...
"	21.6	7.2	80.84	19.16	0.0345	0.0080	0.0269	22.92	77.08	0.0349	0.0787
"	...	7.2	...	100.	0.0115	...	0.0113	...	...	...	...
Citric ...	7.2	...	100.	...	0.3540	0.3521	...	...	...	...	...
" ...	7.2	21.6	34.1	65.9	0.1690	0.0165	0.1461	10.15	89.85	0.1626	0.4785
" ...	...	21.6	...	100.	0.1175	...	0.1264	...	...	...	...
" ...	14.4	...	100.	...	0.4355	0.4348	...	...	...	...	...
" ...	14.4	14.4	60.8	39.2	0.1725	0.0210	0.1355	13.42	86.58	0.1565	0.5439
" ...	...	14.4	...	100.	0.1080	...	0.1111	...	...	...	...
" ...	21.6	...	100.	...	0.4870	0.4875	...	...	...	...	...
" ...	21.6	7.2	80.84	19.6	0.2305	0.0982	0.1221	44.58	55.42	0.2203	0.5946
" ...	...	7.2	...	100.	0.1030	...	0.1071	...	...	...	...

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[1] See page 441.

The alloys Nos. 1 and 2 in the acetic acid were the ones on which the small black crystals before mentioned were found. The crystals on No. 1 weighed 0.0970 gram, and gave on analysis 0.0931 gram of lead, or 91.6 per cent. Those on No. 2 weighed 0.0620 gram, and gave 0.0586 gram of lead, or 94.45 per cent. They were evidently, therefore, crystals of lead. This amount of lead might have been considered as having been in solution, but it is not included in the amount given in the tables. Weber[1] noticed similar crystals in his experiments, and explained their presence by supposing that, at the surface of the liquid where the oxygen of the air and the acid both acted on the metal, so much lead was dissolved that it was precipitated again by the tin of the alloy below the surface. As, in my experiments, the metal was kept entirely covered by the acid, this could hardly have been the case.

The transparent crystals found on the smallest piece of lead in the tartaric acid were nearly, if not quite, insoluble in water. Under the microscope they appeared to be hexagonal and very much like small quartz crystals. They were found, on comparison, to have the same form as crystals of tartrate of lead. From this and from a few qualitative tests I decided that they must be tartrate of lead. The crystals adhered so firmly to the lead that they could not be removed, therefore the loss of weight, as well as the lead in them, could not be determined.

The results of the experiment agree in all essential points with those statements which I have found that have been supported by actual experiment. Those statements which would have us suppose that alloying with tin increased the corrosion of lead seem to be founded on the case of some stray tank or pipe, rather than on a well-conducted research. Moreover it does not appear, as is often supposed to be the case, that the alloy is more acted upon than either of the metals.

It was suggested that the galvanic action would influence more the rapidity of the corrosion than the total amount of metal dissolved; hence that the effect would be more clearly marked at the end of two days than at the end of two weeks, but experiment showed that this is not the case. For this experiment I used only one of the alloys, namely that containing the most tin: the results are recorded in Table II. While the amount of action is not exactly proportional to the time of exposure, it is not far from being so in the case of acetic acid, and in the case of citric and tartric acids it is evident that the action is very slight at first and increases appreciably as time goes on.

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[1] *Loc. cit.*

TABLE II.

Kind of Acid.	Surface exposed, in sq. inches.		Percentage composition.		Loss of weight, in grms.	Found in solution, in grams.		Percentage of dissolved metals.		Total amount dissolved (in grams) from	
	Lead.	Tin.	Lead.	Tin.		Lead.	Tin.	Lead.	Tin.	Alloys.	Pure Metals.
Acetic	7.2	...	100.	. .	0.0515	0.0497	...	...	...	...	...
"	7.2	21.6	34.1	65.9	0.0460	0.0046	0.0387	10.62	89.38	0.0433	0.0896
"	...	21.6	...	100.	0.0400	...	0.0399	...	...	...	...
Tart'c	7.2	...	100.	...	0.0400	0.0374	...	...	...	...	...
"	7.2	21.6	34.1	65.9	0.0120	0.0012	0.0124	8.82	91.82	0.0136	0.0470
"	...	21.6	...	100.	0.0255	...	0.0096	...	...	...	...
Citric	7.2	...	100.	...	0.0625	0.0599	...	...	...	...	...
"	7.2	21.6	34.1	65.9	0.0215	0.0015	0.0218	6.44	93.56	0.0233	0.0817
"	...	21.6	...	100.	0.0120	...	0.0218	...	...	...	...

In these experiments, although the metal was covered with the acid and the beaker with a watch-glass, the air had more or less free access to the surface of the liquid. To see what effect the air had on the corrosion, and to approach more nearly the conditions of a sealed can, I took some glass-stoppered bottles and repeated the experiment in them. I weighed the strips of metal as before and placed them in the bottles, then heated the bottles on steam cups, and while hot filled them with the acid, also heated to boiling to expel any air. The bottles were at once tightly stoppered. As they cooled a few of them leaked a little, but as they were nearly full of liquid very little air could enter. They were put in the same place as in the former experiments and left for two weeks. On being examined at the end of this time there was evidently much less corrosion than in the case of the corresponding experiments in open beakers. There was no discoloration, and no crystals formed. That the air had been pretty well excluded could be seen from the way the stoppers stuck in the bottles even after they could be turned with ease. The same difference in the character of the precipitates of sulphide of tin was noticed as before.

The following table gives the results:

TABLE III.

Kind of Acid.	Surface exposed, in sq. inches.		Percentage composition.		Loss of weight in grams.	Found in solution, in grams.		Percentage of dissolved metals.		Total amount dissolved (in grams) from	
	Lead.	Tin.	Lead.	Tin.		Lead.	Tin.	Lead.	Tin.	Alloys.	Pure Metals.
Acetic	7.2	...	100.	...	0.0900	0.0886	...	...	...	...	...
"	7.2	21.6	34.1	65.9	0.0365	0.0052	0.0289	15.25	84.74	0.0341	0.1332
"	...	21.6	...	100.	0.0430	...	0.0446	...	...	...	...
Tart'c.	7.2	...	100.	...	0.0365	0.0343	...	...	...	...	...
"	7.2	21.6	34.1	65.9	0.0085	0.0018	0.0084	17.65	82.35	0.0102	0.0400
"	...	21.6	...	100.	0.0080	...	0.0057	...	...	...	...
Citric.	7.2	...	100.	...	0.0560	0.0510	...	...	...	...	...
"	7.2	21.6	34.1	65.9	0.0250	0.0018	0.0249	6.74	93.25	0.0267	0.0644
"	...	21.6	...	100.	0.0120	...	0.0134	...	...	...	...

It will be noticed that the corrosion was considerably less. For convenience I give a table showing the comparative results obtained in open and in closed vessels.

TABLE IV.

Dissolved from	By Acetic Acid.		By Tartaric Acid.		By Citric Acid.	
	Open.	Closed.	Open.	Closed.	Open.	Closed.
Lead	0.4216	0.0886	0.0542	0.0343	0.3521	0.0510
Alloy......................	0.3744	0.0341	0.0298	0.0102	0.1628	0.0267
Tin	0.2906	0.0446	0.0212	0.0057	0.1264	0.0134

The acids used were of about the strength of good vinegar. It would naturally be supposed that less strong acids, such as usually occur in canned goods, would cause correspondingly less corrosion. This does not seem to be the case; an incomplete series of experiments seem to indicate that a dilute acid, if used in sufficient quantities, causes much more corrosion than would be inferred from its strength.

To try now the action on the cans themselves, and also the effect of the solder, I took three cans that had been emptied and put 200 cc. of acid into each—acetic acid in one, tartaric acid in another, and citric acid in the third. I covered these cans as well as I could by tying two thicknesses of paper over each, but of course they were practically open cans; moreover, the acid did not nearly fill them. They would represent, therefore, a can that had been partly emptied and set away, rather than a fresh one.

When examined at the end of two weeks, the tinning up as far as the acid reached was entirely taken off, except in the acetic acid. The citric acid had a yellowish color, and a quantity of white powder was deposited on the bottom of the can. I emptied the acid from the cans and added a few drops of chlorhydric acid, fearing that the organic acid was not sufficient to hold up the sulphide of iron. The addition of chlorhydric acid and a little warming dissolved the white powder in the citric acid, and at the same time destroyed the yellow color. On passing sulphuretted hydrogen through the solutions, a very large precipitate was obtained. This I filtered off, washed, and treated with ammonium sulphide; the residue was collected on a filter, dissolved in strong chlorhydric acid, and after evaporation the lead was precipitated as sulphate. The tin was determined in the ammonium sulphide solution. The result was as follows:

Acetic	acid	dissolved	0.4178	gram of tin	and	0.0117	of lead
Tartaric	"	"	1.0430	"	"	0.0873	"
Citric	"	"	0.6828	"	"	0.1559	"

In addition to the lead and tin there was a good deal of iron dissolved.

This shows that corrosion takes place very rapidly after a can is opened, and that a can once opened should be emptied at once. One would have supposed that the acetic acid would have acted more than the others, and it probably would if the conditions in the different cans had been exactly the same. It is probable that more solder was exposed in the cans treated with tartaric and citric acids; at any rate the lead must have come from the solder, as the tin from which the cans were made proved, on being tested, to be free from lead.

On the Quality of Commercial Tin-plate.

Having seen the action of some of the more common vegetable acids on lead and tin, and the alloys of the same, we come to the tin-plate itself.

The tin-plate used in this country is entirely imported, most of it coming from England. The two principal kinds are "Bright plate" and "Terne plate." Bright plate is, or should be, tinned only with pure tin. It is divided into several grades, according to the thickness of the tinning and the quality and heaviness of the iron which forms the basis, but in all these grades the tinning is supposed to be pure tin. Terne plate, on the other hand, is known to contain large quantities of lead, and is often called lead-plate, there being no attempt to pass it for tin, at least by respectable persons.

Tinware and fruit-cans are made from bright plate, while terne plate is used altogether for roofing. Of course the boundaries are sometimes overstepped; those who are very particular use bright plate for roofing, and those who are too avaricious may make tinware out of terne plate. This last, I think, however, is very seldom the case, and the heavy nature of terne plate unfits it for canning.

Knowing these divisions of tin-plate, the questions before us now are: Is bright plate, especially that used in canning, always tinned with pure tin? and how commonly is terne plate used where it will come in contact with food?

I procured some specimens of plate through the kindness of one of the largest importing houses in the city. These I tested by several methods. With the bright plate, taking small pieces, I could find no lead at all, and only after taking half a square foot did I find a trace. This was no more than would be found in most English bar-tin. I now tested a number of cans from various sources, as well as the worst-looking tinware from the so-called 5-cent stores, but not once did I find enough lead to show an intentional adulteration. Neither have I found any well instituted attack on the character of the tin-plate in this country. A good deal has been said and many suspicions thrown out, but the only statements of analyses that I have seen are in a Board of Health report of a Western State.[1] The author found lead so invariably in all tin articles that came into his hands that one cannot help suspecting that the methods of analysis were unreliable. He even observes that he found a considerable quantity of lead in what was sold for pure tin—a thing quite possible, it is true, but not likely to happen with dealers to whom a chemist would naturally go for pure supplies.

Even if the tin of the can is pure, there remains the solder, which always contains a large quantity of lead, and is used very freely. There remains, also, the fact that the vegetable acids act considerably upon tin itself. There are many published statements as to the presence of tin in canned goods, and the careful inspection of the inside of a can which has contained an acid fruit shows quite clearly in many cases that corrosion has taken place. Moreover, although my experiments tend to show that the amount dissolved when the air is excluded is much less than when open, still it is an appreciable quantity; and if, as seems to be the case, the amount increases with the time, that dissolved from an old can must be considerable.[1]

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[1] Mich. Board Health Rept. 1878, p. 29.

The terne plate, which is that most often used for roofing, cannot be considered quite harmless in cases where the water from the roof is used for household purposes. But as the tin roof as well as the whole house is generally covered with a paint containing far more lead than the terne plate itself, it would be absurd to complain while we use white lead to such an extent as at present.

I made a rough analysis of the tinning of terne plate by dissolving it off with chlorhydric acid, precipitating the lead and tin as sulphide and separating them with sulphide of ammonium. The result was as follows: One-fifth of a square foot gave 1.1650 gram of lead and 0.4469 gram of tin, which would make the tinning consist of 72.27 per cent. of lead and 27.73 per cent. of tin. Terne plate can be readily told by its dullness; it comes also in larger sheets than bright plate.

Although constantly on the watch for tinware made of terne plate, I have been able to find none. I am informed on good authority, however, that it is sometimes used for that purpose, but conclude that such use must be rare in this section of the country.

On Commercial Tin-foil.

Tin-foil is so much used now-a-days on chocolate, compressed yeast, cheese, and the like, that I thought the analysis of a few samples might not be amiss. Here at the outset we have a good proof of adulteration, from the fact that the price of most foil is but little more than half the price of pure bar tin.

I collected a number of samples from different importers and manufacturers. They varied greatly in thickness, coloring, and design, but I had reason to suppose that many were the same in composition. I took what I thought was a fair sample of them as regarded composition, and analyzed them.

The method used was that usually used for solders, the oxidation with nitric acid. It was not thought necessary to correct for the trace of lead retained by the oxide of tin; neither were traces of copper or other metals sought for, which even if present would hardly influence the character of the foil, at least as far as sanitary purposes were concerned. The results of the analyses will be found in Table V. I give in the table the size of the piece of foil taken for analysis, its weight, and the weight of the lead and tin found in it, as well as the percentage composition. Only the first three foils were sold for pure tin. Some were sold as "composition foils," but generally, unless special inquiry was made, nothing was said of their composition.

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[1] It is hardly to be supposed that the proportion indicated by the above experiments continues indefinitely.

TABLE V.

No.	Amount taken		Amount found in grams.		Percentage.	
	Size in sq. in.	Weight in grams.	Tin.	Lead.	Tin.	Lead.
1	6	0.2285	0.2275	...	99.53	...
2	6	0.4260	0.4227	...	99.23	...
3	6	0.5950	0.5929	...	99.65	...
4	6	0.5150	0.1162	0.3945	22.56	76.60
5	6	0.9080	0.0902	0.8152	9.94	89.95
6	6	0.7140	0.1642	0.5464	23.00	76.41
7	6	2.0785	0.0839	1.9860	3.86	95.75
8	6	1.8580	0.1172	1.7360	6.31	93.43
9	6	0.3030	0.1125	0.1819	37.44	60.03
10	2.25	0.4720	0.1078	0.3678	22.84	77.94
11	3	0.8005	0.2004	0.5969	25.03	74.55
12	6	1.4940	...	1.2240	...	81.92

In order to see if I had had a fair sample of the foils in general use, and to see which of them were most used on articles of food, I took several foils that had been in actual use and analyzed them. The results appear in Table VI. It will be seen that each corresponds very nearly to some one in Table V. Nos. 21, 23 and 28 were on chocolate; Nos. 22 and 27 on different kinds of compressed yeast; Nos. 25 and 26 on "Neuchâtel" cheese; No. 24 on the outside of a box of troches. No. 23 was on a small cake of chocolate bought at a street stand, while No. 28 was an embossed foil and on a very fashionable cake of chocolate. No. 25 was very brittle and showed signs of being acted upon. The cheese was quite acid to litmus.[1]

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[1] The use of a foil containing about 75 per cent. of lead for wrapping the so-called Neuchâtel and other soft cheese is certainly reprehensible. Owing to the acid in, or developed in, the cheese the foil becomes crumbly, and even when the cheese is first covered with greased paper, particles of the oxidized foil are very likely to become attached to the cheese as it is used. Attention has been repeatedly called to this matter abroad, among others by Wittstein (Dingl. pol. Journ. 208, 341,) who found appreciable amounts of lead in cheese thus wrapped.

TABLE VI.

No.	Amount taken		Amount found in grams.		Percentage.	
	Size in sq. in.	Weight in grams.	Tin.	Lead.	Tin.	Lead.
21	6	0.2650	0.2653	...	100.10	...
22	6	0.5145	0.5130	...	99.70	...
23	6	0.2560	0.2559	...	99.96	...
24	6	1.1175	0.1111	1.0040	9.94	89.87
25	...	1.1600	0.2570	0.8733	22.15	75.27
26	...	0.7915	0.1645	0.5793	20.77	73.19
27	6	0.4435	0.4419	...	99.63	...
28	2	0.4850	0.0938	0.3879	19.34	79.99

MASS. INST. OF TECHNOLOGY, BOSTON, MASS.

REDUCTION OF NITRATES BY FERMENTS.

BY ALFRED SPRINGER.

A year and a half ago, while experimenting with infusions of the roots of plants in water, I noticed a copious evolution of nitric oxide proceed from those rich in nitrates. It immediately struck me that this arose from the action of small organisms which covered the roots of plants. Starting out with this idea, I made separate infusions of the roots, stems and leaves of tobacco, and divided each set into four parts. Fermentation was excited in the first by the addition of small quantities of yeast, in the second by urine, in the third by the so-called spontaneous method, and in the last by the newly-discovered ferment. Not only were the nitrates originally present completely dissociated, but also considerable quantities of freshly added nitrates underwent the same process. All the infusions contained amongst other ferments one special kind, noticeable by its extreme activity. In appearance it closely resembles the butyric ferment, being composed of small cylindrical rods rounded at the extremities, generally isolated, or, when joined, two by two acting as one body. They move rapidly with a wriggling motion and often bend their bodies until they form a perfect circle. Another ferment or modification of the former is present which is somewhat smaller and spins around its smaller diameter as an axis. Phenol has no appreciable effect on the new ferment, and gave the means of partly isolating it from others.

Believing that to this ferment is owing the power of dissociating the nitrates of the soil, I have begun a series of experiments to decide the question.

I give these preliminary statements in regard to my work on account of the experiments lately made in France by Gayon and Dupetit[1] and Deherain and Marquenne,[2] the results of which closely agree with mine as stated at the Ohio Mechanic's Institute a year ago. I also, like the above-mentioned chemists, obtained quantities of butyric acid. There is little doubt but that the ferment mentioned by Béchamp[3] when working with chalk from cretaceous formations instead of pure precipitated calcium carbonate, and by him called *Microzyma cretae*, is the same as the one obtained by me from plant infusions. Perhaps the conflicting descriptions of butyric ferments are often owing to the presence of this widely-spread ferment; which may be either a modification of the butyric ferment caused by abnormal influences bearing upon it, or an entirely different one.

Although it may be classed among the anaerobics, air does not kill it, nor stun it for any length of time. For its greatest activity, temperatures lying between 35° and 40° C., and much water, are most propitious. The great amount of these ferments upon the roots of plants, less on the stems, and least on the leaves, leads me to believe that their presence is some sort of a link between the plants and their nitrogenous constituents. In order to test this hypothesis I have now in my laboratory soil first heated to 120° C., whereby the ferments are killed; this is placed in bottles supplied with air filtered through cotton. In some of the bottles well washed seeds and roots are sown; in some cases the ferments are added, and in others their presence is avoided.

CINCINNATI, *Jan.* 11, 1883.

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[1] Comptes rendus **95**, 644-46. [2] *Ibid.* **95**, 691-93. [3] Bull. Société chimique [2] **6**, 484.

ON THE CONDUCT OF MOIST PHOSPHORUS AND AIR TOWARDS CARBON MONOXIDE.

BY IRA REMSEN AND E. H. KEISER.

Recent experiments have drawn attention anew to the question concerning the existence of an active form of oxygen distinct from ozone, and capable of effecting changes which ozone cannot effect. Hoppe-Seyler[1] and Baumann[2] hold that the oxidizing action of palladium-hydrogen is due in the first instance to the splitting up of the molecule of ordinary oxygen by the active hydrogen, resulting in a momentary liberation of atoms of oxygen which exhibit very active properties. Traube,[3] on the other hand, holds that this action is due to the formation of hydrogen dioxide, and that the oxidizing effects noticed are only those of the dioxide. At first, however, this explanation did not appear probable, for Baumann had shown that palladium-hydrogen in the presence of oxygen has the power of oxidizing carbon monoxide, and one of us[4] had previously shown that hydrogen dioxide has not this power. Traube afterwards conceded this point, but then showed that, while hydrogen dioxide itself has not the power of oxidizing carbon monoxide, it has this power in the presence of palladium. We have repeated the experiment of Traube, and can confirm his statement.[5] From the evidence thus far submitted, Traube's explanation of the oxidizing action of palladium-hydrogen certainly appears to be more probable than that of Hoppe-Seyler.

There is, however, one experiment recorded which indirectly lends some support to Hoppe-Seyler's explanation. We refer to the experiment first performed by Leeds,[6] and subsequently by Baumann,[7] which consisted in bringing air and carbon monoxide together in the presence of moist phosphorus. Under these circumstances, according to both authors, oxidation of the monoxide is effected. Accepting the conclusion, the simplest interpretation of the fact is this: The phosphorus acts upon the oxygen, splitting the molecules, uniting with some of the free atoms and momentarily setting others free. The free atoms then unite with oxygen molecules to form ozone, and with carbon monoxide to form the dioxide. This view is similar to that first put forth by Hoppe-Seyler to account for the oxidizing action of palladium-hydrogen as above related. If, then, the result reached by Leeds and by Baumann is correct, we have some evidence, though it is not conclusive, of the existence under some conditions of a form of oxygen more active than ozone. We say it is not conclusive, for, as hydrogen dioxide is formed under these circumstances, we may assume that the action is due to combined influence of the dioxide and phosphorus.

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[1] Hoppe-Seyler, Zeitschrift für physiologische Chemie, **1**, 396; **2**, 22, 25.

[2] Baumann, *Ibid.* **5**, 244.

[3] Traube, Berichte der deutschen chemischen Gesellschaft, **15**, 659; 2421; 2434; 2854.

[4] Remsen, This Journal, **4**, 50.

[5] We noticed that if a small quantity of free hydrochloric or sulphuric acid is present in the hydrogen dioxide, some of the palladium is dissolved. Similar observations have been made by Fairly (Berichte der deutschen chemischen Gesellschaft, **8**, 1600; **9**, 948), though the statements which we have seen concerning this phenomenon are very meagre.

[6] Journal American Chemical Society, **1**, 232.

[7] Zeitschrift für physiologische Chemie, **5**, 250.

The importance of the subject has led us to repeat the experiments of Leeds and of Baumann, and we have been led to a conclusion directly opposed to that recorded by these authors. As they apparently worked with great care and both agree, it will be necessary for us to describe our work in detail in order that any who may wish to convince themselves may avoid sources of error which have been overlooked in the earlier experiments.

We tried first the effect of passing air alone, freed from carbon dioxide, over moist phosphorus. After its exit from the vessel containing the phosphorus it was filtered through a layer of previously ignited asbestos contained in a tube between two and three feet long, and then into a vessel containing clear baryta water. A precipitate was formed at once, and increased in quantity the longer the current continued. It was tested for phosphoric acid and for phosphorus compounds in general, but not a trace of these could be detected. The passage of air through the apparatus was continued for some days for the purpose of collecting enough of the precipitate for examination and analysis. It proved to be nothing but barium carbonate.

The carbon dioxide must have come from one of two sources, either from some carbonaceous material contained in our phosphorus, or as the result of the action of ozone on the cork stoppers used to make connections. The exposure of rubber had been avoided almost entirely, but still there was some slight opportunity for contact of the ozone with the rubber in consequence of diffusion. As, however, we had here taken the same precautions as in the earlier experiments on carbon monoxide and ozone; as, further, Baumann[1] appears to have experienced no difficulty from the use of rubber joints, it seemed not improbable that the trouble in our experiment was in the chemical condition of the phosphorus. We hence procured specimens of phosphorus from as many different sources as possible, and with each of these repeated the above described experiment, using the same form of apparatus. In every case the precipitate of barium carbonate was obtained, and, as far as could be estimated, in about the same quantity. Attempts were then made to purify the phosphorus. One specimen was placed in hot water under the receiver of an air-pump, and the air exhausted for the purpose of getting rid of any gases which might be contained in the phosphorus. Other specimens were distilled in an atmosphere of pure hydrogen and the vapor condensed in cold water.[2] No matter what process of purification was adopted, the phosphorus acted in the same way after the purification as before.

Attention was now directed specially to the corks and rubber connections. An apparatus was finally constructed in which these were entirely excluded, or, at least, so protected that the ozone could not possibly reach them. Although a number of different forms of apparatus were tried, we need only describe that which we finally decided upon as the best. This consisted of a flask of from three to four litres capacity, provided with a doubly perforated cork stopper. Through this there passed one glass tube reaching to the bottom of the flask, and another reaching only half-way. Outside the flask the shorter tube was connected with the apparatus intended to remove the carbon dioxide from the air, and the longer tube was bent twice at right angles, and then passed through the stopper of a U-tube about eight inches high. Between this U-tube and a second like it, connection was made by means of a doubly bent glass tube. In the flask there were placed usually two or three sticks of phosphorus each three or four inches long, and enough pure water to somewhat more than fill the neck when the flask was inverted. The U-tubes were filled with ignited asbestos, and there was then added some mercury so that when the tubes were inverted, in which position the entire apparatus was placed when in use, the metal covered the corks with a layer from three-quarters of an inch to an inch in thickness. The connecting tubes passed, of course, in each case through the layer of mercury. The vessel containing the clear baryta water was also connected with the last U-tube by means of a mercury joint similar to those above described. The baryta water was protected from the action of the air by placing before it a small U-tube containing potassium hydroxide, and this last tube was connected with an aspirator. Before connecting the bulbs containing the baryta water, air freed from carbon dioxide was drawn slowly[1] through the apparatus. On now connecting with the baryta-water bulbs no precipitate was formed. Even on allowing the air to remain in contact with the moist phosphorus for periods varying from one to twelve hours, no carbon dioxide could be detected. This experiment was tried over and over again at different temperatures, but always with the same result.

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[1] *Loc. cit.*

[2] In this way a new modification of phosphorus, "white phosphorus," was discovered. See next paper.

About one-third of the air in the ozone flask was now replaced by carbon monoxide from which all dioxide had been scrupulously removed. The mixture was allowed to stand for some hours and then drawn through the baryta-water bulbs, when no precipitate was formed. This experiment was repeated a number of times with the same result. In some cases the air and carbon monoxide were drawn together slowly for a long time over the moist phosphorus, but this made no difference in the result. So frequently was the experiment performed, so great were the precautions against error, and so undeniably negative were the results, that, in spite of the explicit statements of Leeds and of Baumann, we do not hesitate to say that carbon monoxide is not oxidized when exposed to the action of air and moist phosphorus. It follows, of course, from this that the action of air and moist phosphorus on carbon monoxide furnishes no evidence in favor of the view that there is an active condition of oxygen distinct from ozone.

Leeds's error is easily explained. In the first place he took no special precautions to protect the corks from the action of the ozone, and in the second place he passed the gases through a filter of moist cotton for the purpose of removing "oxides of phosphorus." Now cotton, as it is usually met with, yields carbon dioxide when subjected to the influence of ozone, so that the carbon dioxide noticed by Leeds was probably the result of the action of ozone on the cotton or the oily substances which always adhere to it. To test the probability of this explanation, we introduced a short plug of cotton into one of the tubes of our apparatus. It having been shown previously that the air drawn through this apparatus contained no carbon dioxide, it was now found that the presence of the cotton alone soon caused the appearance of a precipitate in the baryta water. This experiment was frequently repeated.

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[1] This operation requires care and constant attention. The phosphorus not unfrequently takes fire. In one case in our experience it took fire after having stood quietly and unmolested for several hours.

Baumann describes his experiments thus:[1] "Ein langsamer Strom von kohlensäurefreier Luft wurde durch eine Flasche in welcher sich feuchter Phosphor befindet, und von da in eine zweite Flasche übergeleitet, in welcher die ozonosirte Luft einem etwas langsameren Strom eines kohlensäurefreien Gemenges von 3 Volum Sauerstoff und 1 Volum Kohlenoxyd begegnet; aus dieser Flasche treten die Gase durch klares Barytwasser. Das Barytwasser blieb, nachdem aus dem Apparate selbst erst alle Kohlensäure entfernt war, bei 6-stündigem Durchleiten der Gase völlig klar. Wurde dagegen die Mischung von Kohlenoxyd und Sauerstoff in die Flaschen eingeleitet, in welcher der Phosphor sich befand, und nach unserer Vorstellung aktiver Sauerstoff auftreten muss, so ist das Resultat ein ganz anderes: das vorgelegte Barytwasser wird schon nach kurzer Zeit trübe und im Laufe einer Stunde bildet sich ein reichlicher Niederschlag von kohlensaurem Baryt."

Nothing is said about stoppers or rubber connections, and it is safe to assume that, in the apparatus used by Baumann, ozone came in contact at some points with organic matter. Hence the formation of carbon dioxide is easily accounted for. But to account for the negative result when no carbon monoxide was used is not so easy. It can only be said that, if the ozone formed is not concentrated, the action on organic connections is not marked. Now, if the temperature should happen to be a few degrees lower than the ordinary temperature of rooms, the formation of ozone would be retarded and there might not be formed enough to act perceptibly on the stoppers, &c. The rate of the current of gas is also of importance. The more rapid the current of air passed over the phosphorus the less ozone it contains, and indeed unless the current be quite slow the oxidizing effect of the ozone on the organic connections does not reveal itself by the formation of a precipitate in the baryta water. Whatever the sources of error in Baumann's experiment may have been, we are confident that a repetition with the precautions taken by us will show him that his conclusion is wrong.

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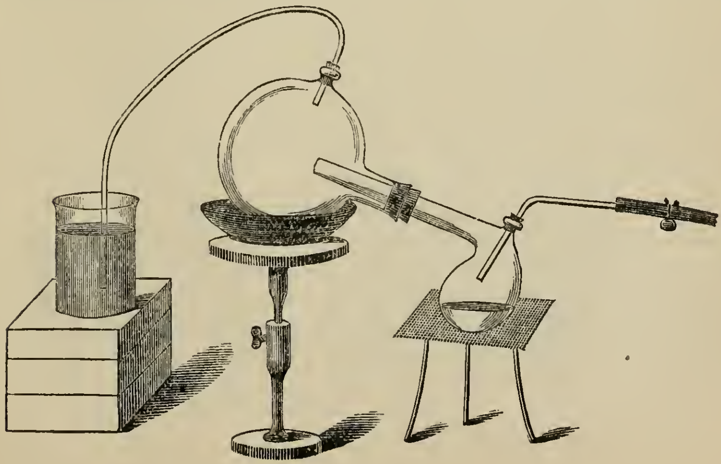
[1] Zeitschrift für physiologische Chemie, **5**, 250.

WHITE PHOSPHORUS.

By Ira Remsen and E. H. Keiser.

In the course of the experiments described in the preceding paper, the suspicion arose that the phosphorus with which we were working might contain some carbonaceous impurity. With the view of removing this if possible, we distilled some of the phosphorus in an atmosphere of purified hydrogen and condensed the vapor on cold water. We were much astonished to find that the substance thus obtained differed very markedly in appearance from ordinary phosphorus, and indeed we thought at first that it could not be the element, but must probably be some new oxide, formed in consequence of a slight leak in the distilling apparatus. It floated on the surface of the water in the receiver, forming a snow white layer about a quarter of an inch in thickness. On examining it more carefully it was found that it was insoluble in water, and could be changed to ordinary phosphorus very easily. The entire quantity obtained in the first experiment happened to be brought into some warm water and was changed at once to ordinary phosphorus. We now endeavored to prepare the substance again, but found considerable difficulty in meeting the right conditions. While we always obtained some of it, we were obliged to make a large number of experiments before the conditions of success became clear. The experiment should be performed as described in detail below.

An apparatus like that roughly illustrated in the accompanying figure should be used.



It is essential that the neck of the retort be inclined upward and that it project well within the receiver. In the receiver there is a layer of ice-cold water from one to one and a half inches deep in the deepest part. In this, lumps of ice are brought, enough to form a fairly compact mass of ice. The receiver rests in a vessel containing cold water. The beaker into which the bent tube dips also contains cold water. Two or three sticks of ordinary phosphorus having been brought into the retort, connection is made by means of the rubber tube with a hydrogen-generating apparatus. The hydrogen is passed first through a solution of potassium permanganate and then through the apparatus as above sketched. As soon as the apparatus is completely filled with the gas the current of hydrogen is stopped by means of the pinch-cock. The distillation is now begun. As soon as the phosphorus vapor reaches the end of the neck of the retort it falls down on the ice and water and forms a white coating. Under some circumstances the material is deposited in piles reaching the height of half an inch to an inch. The principal precaution necessary is to prevent the boiling from becoming so active that the vapor condenses to form liquid just after it leaves the retort neck. In successful operations there will be found at the end a cake of white material floating on the surface of the water, varying in thickness according to the amount of phosphorus distilled. Usually this is quite thin. In order to remove it, it is best to allow the whole apparatus to cool down to the temperature of the air, then to disconnect the retort from the receiver, and put the receiver, with its contents, under water in a larger vessel. In this way the hydrogen can be displaced without danger, and afterwards the white phosphorus can be easily removed. If the above precaution is not taken the receiver becomes filled with a mixture of hydrogen and oxygen while the phosphorus is being taken out, and a little friction may set fire to the phosphorus, thus giving rise to an extremely unpleasant explosion. This actually happened in one of our experiments, and one of us (K.) still carries the marks of the explosion.

White phosphorus is light and plastic. If placed on a piece of bibulous paper so that the water is absorbed from it, it gives off dense white fumes, melts but does not take fire, and is then nothing but ordinary phosphorus. It dissolves readily in carbon bisulphide. It melts at exactly the same point as ordinary phosphorus, and at this point is completely transformed into the latter. From these statements it seems clear that this curious substance bears to ordinary phosphorus much the same relation as "flowers of sulphur" to "roll brimstone." It is in a different physical condition. It is much less susceptible to the influence of sunlight than ordinary phosphorus. We have in our possession some specimens made last October which have undergone very little change, though they have not been specially protected from the action of the light. One specimen, which was purposely placed where the direct sunlight would be upon it for some time every day, has become slightly yellow, but is otherwise, as far as we can judge, quite unchanged. It is still plastic, and when dried acts as above described.

We have not been able to find any references in chemical literature to a substance like that which we have described. The white phosphorus referred to in the communications of Pelouze,[1] H. Rose,[2] Caignard-Latour,[3] Mulder,[4] Marchand[5] and Baudrimont[6] is the coating found on sticks of ordinary phosphorus which have been preserved under water. Böttger[7] also speaks of a variety of white phosphorus prepared by dissolving ordinary yellow phosphorus in alcoholic potassium hydroxide, pouring off the liquid after the phosphorus has become perfectly clear and then adding ice-water. The phosphorus solidifies as a snow-white brittle mass, which can be pulverized under water. From Böttger's description of his product it is evident that it must be quite different from our white phosphorus.

REVIEWS AND REPORTS.

REPORT ON PROGRESS IN PHYSIOLOGICAL CHEMISTRY.

[*Continued from Vol.* 4, 218.]

GASTRIC DIGESTION.

Digestion of Elastic Tissue.—Among the many bodies allied to albumin, elastin, the organic basis of elastic tissue, has long been considered as but partially or with difficulty digestible in gastric juice. Recently Horbaczewski[1] has investigated the subject anew, with quite interesting results. Elastin prepared from the *ligamentum nuchae* of the ox by the usual methods of successive extraction with water, alkali, acid, alcohol and ether, was obtained absolutely free from sulphur, and with the following composition:

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[1] Annales de Chimie et de Physique, **50**, 83.

[2] Poggendorff's Annalen, **27**, 563.

[3] L'Institut, 1834, No. 34.

[4] Journal Pharmacie, **23**, 20.

[5] Journal für praktische Chemie, **20**, 506.

[6] Comptes rendus, **61**, 857.

[7] Journal für Chemie und Physik, **67**, 141, and **68**, 141.

C 54.32, H 6.99, N 16.75.

The finely powdered elastin was readily dissolved and digested by .1 per cent. as also by .2 per cent. hydrochloric acid gastric juice, while in acid of the same strength it remained an equal length of time unaffected. Under the microscope the small fibres were seen to swell up during the first stage of digestion, and to become transparent, similar to shreds of fibrin under like conditions. The old view of the non-digestibility of elastin is undoubtedly dependent on the slowness with which it is dissolved when compared with albumin, and Horbaczewski has found that the rapidity of its digestion stands directly related to the fineness with which it is broken up. .3 gram of finely powdered elastin is completely dissolved in 24–72 hours in 50 cc. of active gastric juice at 40° C.

In order to study the products of digestion, 100 grams of the elastin powder were digested with 1500 cc. of .2 per cent. hydrochloric acid and 1.5 gram of Brücke's pepsin,[2] until the elastin was wholly dissolved. The fluid was then dialyzed until all acid was removed, filtered and evaporated to dryness. A yellowish, gummy powder was obtained, which on further examination showed itself to be composed of two bodies, easily separated from each other. The one was precipitated from its aqueous solution by acetic acid and potassium ferrocyanide or by hydrated lead oxide, and is evidently analogous to the hemialbumose of Kühne and Salkowski. This body Horbaczewski calls hemielastin. Precipitated from its solution by acetic acid and salt and then dialyzed, it shows when dried at 110° C. the following composition:

C 54.22, H 7.02, N 16.84,

by which it is seen that it does not differ from the original elastin. It is readily soluble in cold water, but wholly insoluble in hot, and a very dilute cold water solution is coagulated by long boiling. The hemielastin gives the biuret reaction similar to albumin, likewise the xanthoprotein, only less intense. Hemielastin dried at 100–120° C. loses many of its properties, becoming insoluble in water, shows a marked resistance to the various solvents, similar to elastin, and indeed does not differ in any of its chemical reactions from elastin proper. This makes the third product of digestion which by dehydration can be reconverted into the mother substance. Being amorphous and devoid of the structural elements of the original elastin, it is called *structureless* elastin.

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[1] Zeitschrift f. physiolog. Chem. **6**, 330.

[2] Pflüger's Archiv. **9**, 585.

The second product of the digestion of elastin, the elastin-peptone when freed from hemielastin by carbonate of lead, has the following composition:

C 53.57, H 8.07, N 16.20.

The aqueous solution does not differ in any respect from a solution of albumin peptones, and indeed it would be hardly possible to separate the two. It is thus apparent that elastin, particularly through its digestion products, stands closely related to albumin; the two intermediate products of digestion, hemielastin and hemialbumose, being closely analogous bodies in nearly all of their reactions, while the two end products, the peptones, are equally related. Whether elastin as a constituent of flesh has any importance as nourishment is perhaps questionable. When sufficiently finely divided it is certainly soluble and digestible, and in this condition it is without doubt absorbable. In this connection it may be mentioned that Horbaczewski had an opportunity of studying the digestibility of elastin in the human stomach. 1 gram of elastin powder placed in a small bag of very fine muslin was introduced into the stomach of a hospital patient with an artificial gastric fistula, whose digestion was otherwise normal. After 24 hours it was found that two-thirds of the elastin had disappeared, while a thick swollen mass still remained, which, on treatment with water, yielded a solution giving a strong reaction for hemielastin. Thus here, under not very favorable circumstances, since the powder was swollen to a thick lump, the elastin was digested with a moderate degree of rapidity.

Years ago Schultze[1] observed that when elastin was heated for 30 hours with water at 100° C. in a Papins digestor it was dissolved. The resulting body has ever since been generally considered as pure gelatin from the elastic fibres. Horbaczewski has repeated the experiment by heating 2 grams of powdered elastin with 50 cc. of water in a sealed glass tube for 20 hours at about 100° C. The solution he found to contain a body having all the properties of elastin-peptone, the formation of which we should from analogy naturally expect.

Digestion of Milk in the Stomach.—Uffelman[2] has subjected milk to a careful study in reference to the changes which it undergoes during digestion. He finds that when cow's milk is mixed with .2 per cent. hydrochloric acid in certain proportions, dependent in part upon the amount of water and salts in the milk, a fine granular precipitate is obtained, instead of the ordinary coagulum; thus if 10 cc. of .2 per cent. hydrochloric acid are placed in a cylinder and fresh milk added in quantities of ½ cc., it will be found that when about 7.5 cc. have been added, a fine dust-like precipitate begins to appear, which however is quickly changed into a flocculent one if a few drops more milk are added, or quickly dissolved if a few cubic centimetres of the dilute acid are added. Again, if cow's milk is mixed with .2 per cent. acid in such proportion that the coagulum at first formed is dissolved, viz. 25 cc. fresh milk and 35 cc. .2 per cent. acid, it will be found that even on long standing in an open dish at a temperature of 18–19° C. no change will be noticed other than the formation of a layer of cream. Evidently the proteid matter of the milk in the presence of the acid and possible ferments undergoes a chemical change, although not perceptible to the eye. In fact Uffelman has found by repeated experiment that a mixture of acid and milk in the above proportion standing at the ordinary temperature of a room for 24 hours, yields on an average about .3 gram of peptones. The milk employed in the experiments contained 4.78 per cent. of proteid matter, of which therefore 20–25 per cent. is under these conditions changed into peptones. As is well known milk usually contains a trace of peptones. Pfeiffer[1] however has quite recently found a constant and appreciable "albumin-residue" in the analyses of both human milk and cow's milk which has all the properties of peptones. Precipitated by solution of tannin, it amounts on an average in human milk to nearly .5 per cent., while in cow's milk it is present to the extent of .73 per cent. in milk containing 2.33 per cent. casein and .22 per cent. albumin.

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[1] Annalen der Chem. u. Pharm. **71**.

[2] Studien über die Verdauung der Kuhmilch und über die Mittel, ihre Verdaulichkeit zu erhöhen, Pflüger's Archiv. **29**, 339.

In the artificial digestion of milk with acid and pepsin, Uffelman finds that the rapidity and thoroughness of digestion are greatly influenced by the relative proportion of acid and milk, being dependent on the presence or absence of the thick, cheesy clots of casein; thus in a 4 hours' digestion 25 cc. of milk mixed with 33.5 cc. of a .2 per cent. acid gastric juice yielded peptones corresponding to 81 per cent. of the proteid matter present, while the same quantity of milk mixed with 7.5 cc. of the same gastric juice yielded only 50 per cent. The digestive action is somewhat retarded by the presence of an excess of lactic acid. In regard to the absorption of milk or the products of its digestion, Uffelman has found by experiments on himself and young infants the following results:

Percentage amounts absorbed in a purely milk diet.

	4 weeks old boy.	5¾ months old boy.	11¼ months old boy.	Uffelman
Albumin,	99.20	99.40	98.50	98.70
Fat,	92.20	94.90	93.30	93.40
Salts,	45.40	51.00	57.00	44.20
Sugar,	100.00	100.00	100.00	100.00

As an average of results from four infants, 92.50 per cent. of the milk was absorbed, while in Uffelman's own case only 90.5 per cent. was absorbed. It is thus evident that either from an excess of acid or other cause, a young infant possesses the power of digesting and absorbing milk better than an adult. These results are in close accord with those of Rübner and Gerber.[1]

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[1] Zeitschrift für analytische Chemie, 22, 19, 1882.

METABOLISM.

In 1875 Pflüger[2] advanced the theory that living protoplasm differs in its chemical constitution from dead protoplasm. The albumin molecule, so soon as it becomes a constituent of a cell, as in the brain or muscle, "loses its indifference and begins to breathe, to live." An old and favorite theory for explaining the manner in which food albumin is changed into the cell substance was based upon a possible loose union of the hydroxyl group in the albumin molecule, a general principle according to which many of the known synthetical changes in the body are produced, in a manner analogous to the formation of hippuric acid and other bodies. Pflüger favored the belief that the formation of albumin in the tissues depends upon an ether-like combination of molecules, as in the union of the various parts of the lecithin molecule. Thus albumin passing from the state of dead protoplasm to living, might naturally be expected to show a constitutional difference, and *vice versa.* Pflüger sought for an explanation of the changes which living protoplasm undergoes by a study of the products of animal oxidation, and he was led to the belief that the non-nitrogenous oxidation products obtained outside the body did not differ essentially from those produced in the organism. From which it would follow that living albumin, so far as its hydrocarbon radicals are concerned, does not differ materially from food albumin. But the nitrogen products in the artificial decomposition of proteid matter are quite different. Thus the decomposition products, urea, uric acid and others of regressive metamorphism, notably creatin, guanin, etc., are never obtained artificially from albumin. These latter bodies contain the cyanogen radical, and Pflüger argues that living albumin contains the greater part of its nitrogen in the form of CN and not NH_3, none of the decomposition products containing the former group having ever been obtained from dead albumin. Thus in the formation of living protoplasm from food albumin a change is effected in which the nitrogen atoms pass into the cyanogen compounds, and, on the death of the protoplasm, again return to the more stable condition of amides. Hence, according to the views of Pflüger, the ready decomposition of living protoplasm is to be sought for in the presence of the cyanogen group. Quite recently Loew and Bokorny in a series of interesting papers[3] have advanced the idea of a different structure of the albumin molecule, and like Pflüger have attempted to establish a chemical difference between living and dead protoplasm. These investigators consider "albumin like sugar as a condensation product of bodies of a comparatively simple constitution." Loew's view is that the CHOH group, an isomer of formaldehyde or methyleneoxide, serves as the material for building up the albumin molecule; the aldehyde group itself being possibly formed from various allied substances, such as acetic and tartaric acids, by "*pilz*" growth. For the detection of the aldehyde groups in living albumin Loew and Bokorny experimented mostly with needle-like algae, particularly the various species of Spirogyra and Zygnema, although like results were obtained with other algae such as Vaucheria and Cladophora. Sections from Salix and Syringa also gave satisfactory results, likewise leaves from Valisneria. While various reducing solutions were employed in the reactions, most of the results were obtained with an ammoniacal solution of silver nitrate mixed with potassa and containing 1 part of $AgNO_3$ in 100,000 parts, from which living cells separate the silver while the dead ones do not. The reducing action of the living protoplasm is best shown by placing portions of the cellular algae in a large quantity of the reagent and allowing them to remain there for several hours; if heated to 30° C. the action takes place much quicker. Under the microscope the plasma of the needles is seen to be quite black from reduced silver, while the single cells show numerous black dots or large lumps of silver. The reduction is particularly noticeable in those parts of the protoplasm where the greatest activity would be expected, as in the chlorophyll granules and at the ends of the cylindrical tubules. This reduction of silver is what Loew and Bokorny call the "reaction of life," and really constitutes the only evidence of the existence of aldehyde groups in living protoplasm. In dead cells, however, such reducing action cannot be obtained. Thus in the case of the cellular algae, death of the protoplasm was induced by all possible methods, such as starving, drying, exposure to high temperatures, electrical shocks, mechanical pressure, poisons, anaesthetics, etc., and in nearly every case these methods were sufficient to prevent the reducing action: thus a thread of Spirogyra heated at 50° C. for five minutes or dried between blotting-paper and then exposed to ether vapor for an hour, completely lost the power of reduction. Quinine solutions, however, although they completely disintegrate protoplasm, do not prevent the reducing action from taking place. That the various methods used in the killing of the protoplasm do not remove any possible reducing substances present in the tissue, is plainly apparent from the fact that cells killed by simple pressure lose their power of reducing the silver solution as completely as by more certain means of death, although it must be confessed that it is difficult to understand how the aldehyde group can be broken up by simple pressure, if that is to be inferred. Having thus established the existence of a chemical difference between living and dead protoplasm, Loew advances next to the probable constitution of the albumin molecule. Starting with the idea that an isomer of formaldehyde is the probable antecedent, he considers three successive stages necessary for the construction of the completed molecule. In the first, four aldehyde groups are necessary together with one molecule of ammonia, by the combination of which a body can be formed in which the numerical proportion of carbon to nitrogen would be as 4 : 1, and which would therefore by condensation be able to furnish the albumin molecule,

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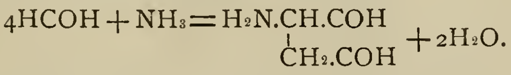
[1] Zeitschrift für Biologie, 1880, 16.

[2] Ueber die physiologische Verbrennung in den lebendigen Organismen, Pflüger's Archiv. **10**, 251. Also abstract in Jahresbericht der Thierchemie, **5**, 238.

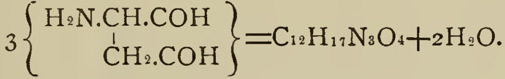
[3] Eine Hypothese über die Bildung des Albumins, Pflüger's Archiv. **22**, 503, 1880. Eine chemischer Unterschied zwischen lebendigen und todten Protoplasma, Pflüger's Archiv. **25**, 150, 1881. Ueber das absterben pflanzlichen Plasmas unter verschiedenen Bedingungen, Pflüger's Archiv. **26**, 50, 1881. Einige Bemerkungen über Protoplasma, Pflüger's Archiv. **28**, 94, 1882. Ueber die Aldehydnatur des lebenden Protoplasmas, Ber. d. deutsch. chem. Gesell. **14**, 2508. Die chemische Ursache des Lebens, Munich, 1881. Die chemische Kraftquelle im lebenden Protoplasma, Munich, 1882.



$$4HCOH + NH_3 = \begin{array}{l} H_2N.CH.COH \\ \qquad\quad | \\ \qquad\quad CH_2.COH \end{array} + 2H_2O.$$

Loew then calls attention to the fact that asparagin, as an important constituent of certain plants, might naturally be connected, at least indirectly, with the formation of albumin, and in the above condensation the product obtained would be an aldehyde of aspartic acid, a body not yet however produced. If ultimately it be proven that albumin is simply a condensation product of an aldehyde of aspartic acid, the formation of albumin from asparagin in the animal kingdom would, as Loew remarks, be hardly more remarkable than the formation of fat from sugar.

The second step in the production of albumin is represented as follows:

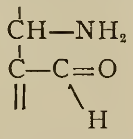


$$3\left\{\begin{array}{l} H_2N.CH.COH \\ \qquad\quad | \\ \qquad\quad CH_2.COH \end{array}\right\} = C_{12}H_{17}N_3O_4 + 2H_2O.$$

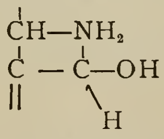
In this condensation, only two of the six COH groups are broken up, and thus a still further condensation is possible. This Loew considers is brought about by reducing influence and the introduction of sulphur, by which Lieberkühn's formula of albumin could be obtained as follows:

$$6C_{12}H_{17}N_3O_4 + H_2S + 6H_2 = C_{72}H_{112}N_{18}SO_{22} + 2H_2O.$$

There are thus, as the developed formulae plainly show, 12 aldehyde groups in the completed albumin molecule, the other 12 passing into the CHOH group by the taking on of 1 atom of hydrogen. The presence of these aldehyde groups, with their great energy, causing "intense motion in the albumin molecule," is, in Loew's opinion, "the cause of life," and in order to represent the chemical difference between living and dead protoplasm, the terms *active* and *passive* albumin have been proposed, the constitution of the individual groups in the two forms being represented as follows:



Group in active albumin.



Group in passive albumin.

It is undoubtedly true that Loew's somewhat fanciful arrangement of the atoms in the complex albumin molecule coincides with the fact that asparagin is one of the principal products of proteid decomposition in plant life, and moreover the formation of asparagin would thereby be readily explainable. Again, Schultze's statement that much more asparagin is formed in nature than is found in the decomposition of albumin by acids, would favor the idea that the decomposition of albumin in the cells is a process of quite a different character. In a like manner the proposed constitutional formula would account for the formation of the saccharine groups found by Schützenberger[1] in the decomposition of albumin, and also the peculiar formation of glycogen in the animal body after a purely albuminous diet. While these latter views are wholly theoretical in their nature, and perhaps hardly worthy of credence in their entirety, there is at least a grain of wisdom in them, and surely nothing which promises to throw any light upon the complex metabolism of protoplasmic matter is to be cast aside without careful scrutiny. It is only to be regretted that there are not more facts at our disposal to sustain Loew's ingenious theories. Since Loew and Bokorny's first papers were published, Reinke[2] has given an account of the presence in chlorophyll plant cells of an aldehyde-like body of great volatility and energetic reducing power both towards alkaline silver and copper solutions. Reinke considers this body to be formaldehyde, which, according to A. Baeyer's view, is the first assimilation product formed in green plants. By distillation of the neutralized juices from plants containing chlorophyll, Reinke obtained in the first few cubic centimetres of the distillate the above-mentioned reducing substance, while plants free from chlorophyll failed to yield any, from which Reinke inclines to the view that this body is the source, in part at least, of Loew and Bokorny's aldehyde reactions in living protoplasm.[3]

R. H. CHITTENDEN.

(*To be continued.*)

ANALYTICAL CHEMISTRY.

Antimony.—"Volumetric Estimation of Antimony in presence of Tin." By E. F. Herroun.[4] The process which is applicable to alloys such as Britannia or type metal, depends upon the fact that antimonic chloride is reduced to antimonious chloride by hydriodic acid with liberation of iodine, while stannic chloride is not reduced. The alloy, in a state of fine division, is dissolved in strong hydrochloric acid with the aid of heat and with frequent additions of small quantities of potassium chlorate. After the metal is entirely dissolved a piece of potassium chlorate is added to insure the conversion of the antimonious chloride into antimonic chloride, and the solution gently boiled until all the oxides of chlorine have been expelled. The solution is then allowed to cool, and a slight excess of a strong solution of potassium iodide added. The free iodine is then estimated by means of a standard solution of sodium hyposulphite.

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[1] This Journal, **2**, 209.

[2] Bericht. d. deutsch. chem. Gesell. **14**, 2144.

[3] In Pflüger's Archiv. **29**, 400, 1882, Bauman, of Berlin, criticises Loew and Bokorny's views, purely, however, on theoretical grounds.

[4] Chemical News, **45**, 101.

If iron, or any other metal whose perchloride is capable of liberating iodine, be present in the alloy, the tin and antimony may be separated by conversion into their oxides by treating the alloy with nitric acid.

A. Weller[1] has made use of the same principle in determining antimony. But his process differs from that of Herroun in the manner of determining the amount of liberated iodine. In Weller's process the iodine is distilled off from the antimonious chloride, collected in potassium iodide and estimated volumetrically by means of sulphurous acid and a standard iodine solution. A number of analyses are given in support of the method. Weller claims priority for the discovery, because his work was done in 1879 and 1880.

Bismuth.—"Volumetric Estimation of Bismuth in the form of Oxalate." By Pattison Muir and C. E. Robbs. The authors described a method[2] for estimating bismuth by precipitation as neutral oxalate, and conversion into the acid oxalate, by washing with boiling water. This process involves boiling the precipitated oxalate for some little time with successive quantities of water, collection and complete washing of the acid oxalate, and its solution in acid, before titration with potassium permanganate. They now propose to make use of the double salt of potassium and bismuth, obtained by adding normal potassium oxalate to a solution of bismuth containing acetic acid and nearly free from mineral acid, and which has the formula $Bi_2(C_2O_4)_3.K_2C_2O_4$ according to Reis.[3] The solution of bismuth is evaporated nearly to dryness, dissolved in nitric acid, evaporated nearly to dryness again, then an excess of glacial acetic acid added, and the whole transferred to a measuring flask. About twice as much potassium oxalate as bismuthous oxide is added, and the flask filled to the mark with acetic acid (1 : 1). The liquid is shaken and allowed to stand for some time, then filtered through a dry filter, and the residual oxalate determined by titration with permanganate. When a large excess of potassium oxalate is used the results are invariably too low, unless a large quantity of glacial acetic acid is added; the double oxalate being soluble in an excess of potassism oxalate, but is reprecipitated by addition of much strong acetic acid. It is best to run in the potassium oxalate from a standard solution in a burette in small successive quantities;

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[1] Liebig's Annalen der Chemie, **213**, 365.

[2] Journal of the Chemical Society, 1878, p. 70.

[3] Berichte der deutschen chemischen Gesellschaft, **14**, 1172.

when the precipitation is apparently complete a few cubic centimetres more are added.

In applying this process to the determination of bismuth in mixtures, it is necessary that the bismuth should be separated from other heavy metals; this may be done by precipitation as oxychloride. The bismuth also should be obtained as nitrate with a small excess of nitric acid.

Zinc.—M. Schroeder[1] recommends the use of thallium instead of lead or cobalt paper in the volumetric determination of zinc by means of sodium sulphide. It is more sensitive than cobalt paper, and is to be preferred to lead paper because it is not affected by zinc sulphide, provided the amount of free ammonia present is extremely small. The amount of ammonium chloride present is of little significance in the use of this indicator.

Cadmium.—Anton Orlowski[2] recommends two different methods for the detection of cadmium in the presence of copper.

First method: After the separation of bismuth hydroxide by means of ammonia, the blue solution is acidified with hydrochloric acid and treated with stannous chloride until the color disappears; milk of sulphur is then added and the liquid heated to boiling. By this means all of the copper is precipitated as black cuprous sulphide. The precipitate is separated by filtration and an excess of ammonia added, which precipitates the tin as stannous hydroxide while the cadmium remains in solution. A yellow precipitate produced by ammonium sulphide in the filtrate indicates the presence of cadmium.

Second method: This is the same as that proposed by G. Vortmann[3] in which copper is precipitated as sulphide by means of hyposulphite of sodium. Orlowski remarks that he had not seen the article of Vortmann until his own was ready for publication.

Silver.—Jean Krutwig[4] finds that traces of silver in lead ores may be quantitatively as well as qualitatively determined in the following manner: 20 to 25 grams of the lead ore are decomposed in an iron crucible with borax, soda and cream of tartar. The lead thus obtained, which contains besides iron and sulphur all of the silver, is dissolved in concentrated nitric acid, water added and the lead sulphate filtered off. The filtrate is then treated with an excess of caustic soda and allowed to stand for some time. The brownish yellow precipitate containing iron, lead and silver is filtered. This precipitate, which consists of lead and iron hydroxide and a so-called plumbite of silver, is then treated on the filter with a somewhat concentrated solution of ammonia, which dissolves the plumbite of silver. The ammonia is expelled from the filtrate by evaporating on the water-bath and the residue dissolved in nitric acid. The silver is then detected in one of two ways: either by treating with caustic soda solution and thus obtaining the characteristic precipitate of silver plumbite, or by precipitating the lead as sulphate, filtering and treating the filtrate with hydrochloric acid.

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[1] Berichte der deutschen chemischen Gesellschaft, **15**, 262.
[2] Zeitschrift für analytische Chemie, **21**, 214.
[3] This Journal, **3**, 229; Zeitschrift für analytische Chemie, **20**, 416.
[4] Berichte der deutschen chemischen Gesellschaft, **15**, 307 and 1264.

Wöhler,[1] in 1837, published a short notice on the fact that caustic soda precipitates a silver and lead compound from solutions of these metals; but since Krutwig's determinations of the composition of this substance do not agree with those of Wöhler, he gives the results of his analyses, which indicate the formula PbO_2Ag_2, and this he calls *silver plumbite.* The silver in this compound may be satisfactorily determined by precipitating with hydrochloric acid and washing with hot water to remove the lead chloride, or by electrolysis in cyanide of potassium solution. When silver is present to the extent of only 0.001 gram the method is not applicable.

Krutwig has also successfully applied Luckow's[2] qualitative method of electrolysis (in ammonia or ammonium carbonate solutions) to the quantitative determination of silver by adding ammonium sulphate to the ammoniacal silver solution.

Nickel and Cobalt.—A. Jorissen[3] recommends, for the separation of small quantities of nickel in the presence of cobalt, treatment of the solution with caustic soda, then with a few drops of bromine water, and finally with a few drops of potassium cyanide solution. The nickel hydroxide is reduced and dissolved, while the cobalt precipitate is not affected even by an excess of the potassium cyanide, but remains suspended in the liquid in the form of black flakes.

If much nickel and little cobalt are present, the latter likewise goes into solution.

Chromium.—Ad. Carnot[4]: "On chromium phosphate and its utilization in analysis and industry."

According to the author, chromium in its chlorides, sulphates or acetates (either green or violet), but not in its oxalates, may be expeditiously and satisfactorily determined as follows: a weakly acid solution of the chromium salt is heated to boiling, and an alkaline phosphate and sodium acetate are added; all the chromium is precipitated as phosphate. The method is equally applicable to chromates; in this case sodium hyposulphite is added as a reducing agent.

The precipitate is washed with a hot solution of sodium acetate, and then with ammonium nitrate. The method is specially valuable in operating in presence of chlorides and sulphates.

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[1] Poggendorff's Annalen, **41**, 344.

[2] Zeitschrift für analytische Chemie, **19**, 1.

[3] Zeitschrift für analytische Chemie, **21**, 208.

[4] Bulletin de la Société chimique, **37**, 482.

F. P. Treadwell:[1] "On the determination of chromium." Th. Wilm[2] has observed that determinations of chromium as oxide give too high results when the precipitation with ammonia is effected in *glass vessels;* results obtained by him in potassium bichromate are: (Cr_2O_3) 55·76, 57·89, 53·92, 55·32, 54·92; calculated, 51.82. Treadwell has therefore made determinations both in glass and in platinum, and his results are satisfactory in either case as shown by the following figures: in glass (Cr) 35·48, 35·49, 35·46, 35·47; calculated 35·54. He accounts for Wilm's results by saying that the glass used by the latter may have been of poor quality. Wilm also stated that chromic oxide ready for final weighing contains chromate; Treadwell finds this to be true, but states that the amount is so small that it cannot be weighed.

M. Richter[3]: "On the alkalinity of potassium chromate." Also, "On a new volumetric method for the determination of potassium bichromate and application of the same as a titrating substance for caustic alkalies."

Richter has found that the apparent alkalinity of potassium chromate when tested with litmus is due to the oxidation of the coloring matter, and not to true alkalinity. Phenolphthaleïne is not affected by the chromate; but if a trace of alkali be added, the real alkalinity thus produced is rendered immediately apparent by the change in color of this indicator. On this fact he bases a method for determining bichromates. To determine both chromates and bichromates in any neutral solution, the bichromate is first estimated by means of a standard solution of an alkali with use of phenolphthaleïne as an indicator; the whole chromic acid is then precipitated in a measuring flask by means of a standard solution of silver nitrate, which is added in excess, and its quantity ascertained by estimating the excess of silver in a measured portion of the liquid. The bichromates may be employed for the volumetric determination of the caustic alkalies and ammonia.

B. Reinitzer[4]: "Studies on the conduct of the acetates of chromium, iron and aluminium."

The results of Reinitzer in this investigation are valuable, not only in their bearing on analytical chemistry, but also because they seem to settle in a satisfactory manner certain previously doubtful points relating to the pure, individual substances. The most complete text-books contain insufficient statements in regard to the acetate of chromium, which, owing to the manifold analogies existing between chromium, aluminium and iron, might be expected to conduct itself similarly to the acetates of the two latter metals. If a solution of chromium sulphate or chloride is treated with an excess of sodium acetate solution and boiled, no precipitate separates out, however concentrated the solution or great the amount of sodium acetate used may be. When boiled, even for a short time, the solution on cooling assumes a violet color, and the properties of the chromium solution are now found to have been strikingly changed. The caustic alkalies, ammonia, ammonium sulphide, alkaline carbonates, and various other reagents now fail to produce in the cold solution even the slightest turbidity. It was found, further, that this chromium solution imparts to a certain amount of iron or aluminium acetate the same passive condition towards the above reagents; and, as a result of this fact, that the method of separating iron and aluminium from other metals which is based on the precipitation of these metals as basic acetates, becomes inapplicable in both qualitative and quantitative analyses whenever chromium salts are present.

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[1] Berichte der deutschen chemischen Gesellschaft, **15**, 1392.

[2] *Ibid.* **15**, 2223.

[3] Zeitschrift für analytische Chemie, **21**, 204.

[4] Monatshefte für Chemie, **3**, 249.

In order to further investigate these phenomena, the acetate of each of the three metals was prepared in pure condition, and its conduct, both alone and in mixtures, examined. The preparation of pure acetate of chromium was attended with difficulties, but was finally effected through the double decomposition of lead acetate and chromium sulphate, the latter having been prepared from purified commercial chromic acid by treatment with sulphur dioxide.

The concentrated solution of lead acetate was added in slight excess to the solution of chromium sulphate, and the mixture allowed to stand for several days to effect a more complete precipitation of the lead sulphate. The excess of lead was then precipitated by sulphuretted hydrogen, the excess of which was afterwards removed by means of a current of carbon dioxide. The solution of chromium acetate thus obtained is violet in color, but yields, on being evaporated to dryness on the water-bath, a green residue, which, when redissolved, produces a green solution. If this green solution is boiled with sodium acetate it becomes purple violet on cooling. Both of these modifications of chromium acetate show in themselves as well as towards reagents the same conduct as the chromium salts of inorganic acids when the latter are boiled with sodium acetate. This fact of the passive condition of chromium acetate explains why, in the quantitative analysis of chromates, the solution, after reduction with sulphuric acid and *alcohol*, must be evaporated to dryness before the chromium can be precipitated by ammonia.

Pure ferric acetate was prepared by precipitating the hydroxide with ammonia in the cold, washing with hot water until no trace of ammonia or chlorine could be detected in the filtrate, and then dissolving in acetic acid. Contrary to all previous statements and contrary to the author's explanation, the clear blood-red solution thus obtained can be evaporated on the boiling water-bath to dryness without furnishing an insoluble residue. If the heating of the dry substance on the water-bath is continued for a time, the metahydroxide can be subsequently precipitated from its solution by means of sodium acetate or hydrochloric acid; if the heating is continued an hour or two the residue becomes insoluble in water.

Very few chemists appear to have obtained perfectly pure ferric acetate; for in all chemical books it is stated as characteristic of ferric acetate, that the iron is precipitated as basic acetate when dilute solutions of it are boiled. This is not true of the pure salt. If, however, an alkaline acetate is added, precipitation is readily effected.

Aluminium acetate was prepared by dissolving the sublimed chloride in water, precipitating from the hot solution with ammonia, dissolving in sulphuric acid and treating with lead acetate, the excess of lead being removed with sulphuretted hydrogen. The solution thus obtained cannot be evaporated on the boiling water bath without giving an insoluble residue. It differs, therefore, in this respect from the acetates of iron and chromium. It is, however, only after a certain concentration has been obtained that a basic acetate separates out. If the water lost by evaporation is continually replaced no precipitate of basic acetate takes place, provided no alkaline acetate is present.

The following statements give the results obtained by mixing the acetates:

If a solution of *green* chromium acetate is treated with a little acetate of iron and the mixture boiled, the iron is deposited as a flocculent precipitate. If the iron acetate is in excess and the green chromium acetate gradually added to it, the solution is maintained up to a certain point when a part of the iron is precipitated.

If however a solution of chromium acetate which was originally *violet*, is treated with acetate of iron, no precipitation takes place, even though the quantity of iron salt added is large and the boiling is long continued.

The amount of iron acetate which becomes passive through the influence of chromium acetate depends upon various conditions; such as the amount of the iron acetate, the concentration of the liquid, whether the two are brought together when cold or hot, etc. Detailed experiments are described showing the effect of these conditions.

The effect of chromium acetate on aluminium acetate is in general the same as on iron acetate, except that aluminium acetate can not be precipitated by *green* chromium acetate.

Tin.—M. M. P. Muir[1]: "Detection of tin in presence of antimony." The mixed sulphides are dissolved in strong hydrochloric acid, and the stannic reduced to stannous chloride by boiling with copper turnings, after which the presence of tin can be detected by adding mercuric chloride.

Uranium.—Clemens Zimmermann[2]: "Investigations on Uranium." In 1846 Margueritte published a description of the now well-known volumetric method for the quantitative determination of ferrous salts which depends upon the reduction of potassium permanganate. Until 1861 this method was applied indifferently to solutions containing either sulphuric or hydrochloric acid. Löwenthal and Lenssen at this time showed conclusively that if hydrochloric acid be present in the solution, chlorine is liberated, owing to the oxidizing action of the permanganate, and that errors are thereby introduced. Fresenius verified these conclusions and recommended the use of sulphuric acid when possible, and in other cases the following modification, *i. e.* the ferrous solution is diluted to ¼ litre; of this 50 cc. are added to a larger amount of water acidified with H_2SO_4 and the solution titrated with permanganate; then 50 cc. more are added and a second titration effected, also a third and fourth. The results of the third and fourth determinations are found to be correct.

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[1] Chem. News, **45**, 68.

[2] Annalen der Chemie, **213**, 285.

Zimmermann now modifies the Margueritte method by introducing into the ferrous solution *containing hydrochloric acid* manganous sulphate, which prevents the liberation of chlorine, and consequently the errors known to exist when the manganous salt is not used.[1]

The manganous sulphate solution is obtained by dissolving 100 grams of the salt in water and diluting to about 500 cc. 20 cc. of this solution are sufficient even in presence of 50 cc. hydrochloric acid (1.12 sp. gr.) to render the results of the titration of ferrous salts by potassium permanganate absolutely exact. The permanganate is added slowly with constant stirring.

Zimmermann also applies this method to the volumetric determination of uranous salts. If uranic salts in solution be treated with sulphuric acid and zinc they are converted into uranous salts and the reduction goes no further.

For the determination of uranous salts Zimmermann has also proposed the following method: An acid solution of potassium bichromate oxidizes uranous salts just as quickly and perfectly as potassium permanganate; moreover, it liberates iodine from potassium iodide; the liberated iodine can then be converted into sodium iodide by means of sodium hyposulphite. Accordingly, to determine uranium, the reduced salt in solution is acidified with hydrochloric acid, then an excess of a solution of potassium bichromate of known strength is added, and the whole diluted with water to about 150 cc., and with constant stirring a solution of potassium iodide is added.

The iodine liberated is determined by means of a standard solution of sodium hyposulphite with use of starch solution. Finally, an iodine solution of known strength is added until the formation of the blue iodine-starch compound is noticed. The results thus obtained agree closely with those obtained by the Margueritte method.

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[1] It is now clear that the correct results obtained by Fresenius in the third and fourth repetitions of the titration are due to the accumulation of *manganous* compounds in the solution in which the determination is being made.—H. N. M.

Molybdic Acid.—Otto Freih. v. d. Pfordten:[1] "Volumetric method of determining molybdic acid." Molybdic acid is quickly reduced by zinc and hydrochloric acid. The following method is analogous to Zimmermann's method for uranium (see above).

The salt to be determined is dissolved in a little water and 60 cc. of a 27 per cent. hydrochloric acid are added; 8 to 10 grams of zinc in sticks are then introduced (the amount of iron in which has been previously determined by titration). When the liquid has become yellow in color, and before the zinc is completely dissolved, the vessel is cooled; the liquid is then transferred to a porcelain dish, in which are contained dilute sulphuric acid and manganous sulphate, and titrated with permanganate, with active stirring, until a rose tint appears.

W. C. D.

NOTES.

Filtration Balance.

All the arrangements for the automatic washing of precipitates, of which I have seen previous mention, provide for keeping the water at nearly a constant level in the funnel. By this method of washing a precipitate, usually much more water is necessary than if each portion of water is allowed to drain off before a new addition of it. At the Cincinnati meeting of the American Association for the Advancement of Science in 1881, Prof. H. Carmichael, of Bowdoin College, Maine, exhibited a filtration and evaporation balance, which I must describe before giving my modification of it. The figure, without the upright CD, illustrates this balance, which is most convenient for delivering a large amount of liquid on a small filter or into a small evaporating dish.

A beam AB balanced on the knife-edge (or pivot) C, supports in a ring, A, the funnel which is equipoised by the weight V. *s* and *r* are corks passed through the upright NL, and hold in any position the tubes U and T, which are bent to pass through them. Close to C, and under the beam, passes a rubber tube *e*, which connects the tubes U and T and conducts the wash-water or other liquid. By use of thumbscrews *g* and *k* the little brass arms *f* and *i* may be raised to adjust the pressure upon the rubber tubes *e* and *h*.

To the above-described apparatus, I add a vertical rod CD fastened to the arm AB and at right angles to it; on this is supported a weight W, whose height is fixed by the binding screw also sliding on this rod. I employ for two-inch funnels a cylindrical lead weight V, weighing about 300 grams; for three-inch funnels about 500 grams. The apparatus is used as follows:

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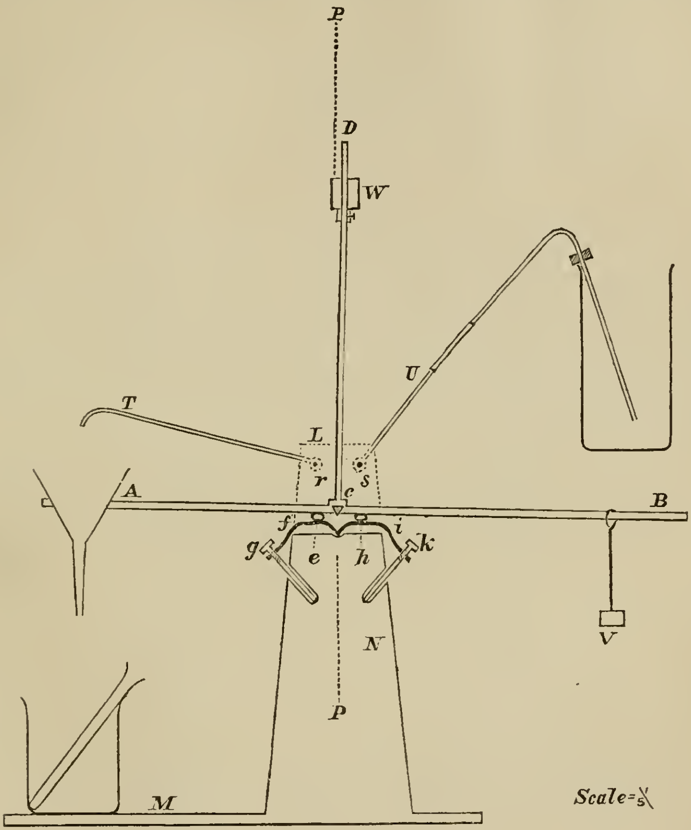
[1] Berichte der deutschen chemischen Gesellschaft, **15**, 1925.



Having brought all the precipitate on the paper in a funnel, allow it to drain, put the funnel in place and fix the weight W near D, then slide the weight V on B until it will just be able to raise A from its lowest position, when of course W will move to the right of the vertical PP. Then water will pass through *e* and drop into the funnel until it is nearly full, when (if W and *k* are adjusted properly), A will fall, bringing W to the left of the vertical, and in this position no water will pass through *e*. When the funnel has again drained, the arm A rises, and (the water again flows into the funnel) this alternating motion continues so long as water is supplied. I have made AB of iron 10x4 mm. The upright NL is 35 mm. thick; other dimensions may be taken from the figure.

It is essential that the tube *e* admits of being closed by very gentle pressure (less than 100 grams) of the knife-edge cut on the under side of the beam. I use for this pure rubber tubing 2.5 mm. exterior diameter.

Removing W the apparatus may be used as was intended by Prof. Carmichael. When conducting an evaporation, the dish rests in A and the gas passes through *h* to the burner, so that when the liquid is exhausted, and before that in the dish has come to dryness, the arm A will rise, compress *h*, and so extinguish the flame.

F. P. DUNNINGTON.

UNIVERSITY OF VIRGINIA, *January*, 1883.

Helvite from Amelia County, Virginia.[1]

Helvite has been recently found in small quantity by H. C. Lewis at the Mica Mines, near Amelia Court House, Virginia. It occurs in small sulphur-yellow crystals and crystalline masses associated with orthoclase and garnet. An analysis of the carefully picked mineral was made by R. Haines with the following results: Specific gravity 3.29.

SiO_2	32.32
BeO	11.47
Al_2O_3	2.68
MnO	45.38
FeO	1.85
CaO	.64
K_2O	.39
Na_2O	.92
S	4.50
H_2O	.30
	100.45
Less oxygen replaced by sulphur	2.25
	98.20

The glucina was separated by boiling with NH_4Cl (Berzelius's method). For the estimation of SiO_2 two portions of the mineral were taken, one of which was treated in the usual way for the total silica, and the other, while still moist, was treated several times with a boiling concentrated freshly made solution of sodium carbonate, and the washed residue weighed. This residue (in the analysis above given) of 9.22 per cent. was considered to be silicious gangue (insoluble silicate), and the difference from total silica to be the true gelatinous silica of the mineral species. Accuracy of this determination being doubtful, owing to the very small amount of the mineral at command, a second determination was made on larger quantities (1 gram and ½ gram) also carefully picked from another sample of the mineral received later. In this was found total SiO_2 32.49 per cent., of which 5.19 per cent. was insoluble gangue.—(*Journal of Franklin Institute*, July and October, 1882.)

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[1] Abstract furnished by the author.

Water Analysis.[1]

For the ammonia method of water analysis, R. Haines recommends the following working details supplementary to the directions of Wanklyn.

The glass retort should have its neck sufficiently narrow to be thrust easily five or six inches within the tube of the Liebig condenser, and a short piece of wide rubber tubing slipped up the retort neck should connect them.

Before connecting, cleanse retort with strong H_2SO_4, and also, if necessary, with strong HCl, and wash thoroughly every part of the apparatus. After connecting, flush the whole apparatus with clean tap water introduced at tubulum of retort, and remove water from retort by a glass syphon. By removing the permanganate solution with the syphon, and repeating the flushing with water after each analysis, it will not be necessary to disconnect the apparatus for a considerable time in the case of most potable waters. Violent bumping sometimes occurs during distillation, even of pure soft spring waters as well as some very impure waters. Disasters from this cause are best avoided by quickly removing the burner from below the retort until the foam subsides, and by regulating the flame by a screw compressor. Introducing ignited pumice, &c., tapping or shaking the retort or inclining the retort upward, are not to be recommended. The current of water passing through the condenser must be constant and sufficiently rapid. The distillation should invariably be continued until less than .005 mgm. NH_3 is found in 50 cc. of distillate, both of free and albuminoid ammonia. In highly ammoniacal waters the free ammonia is best distilled off in one portion of 200 or 250 cc., which is diluted and an aliquot part nesslerized. Such waters sometimes yield considerably more than three-fourths of their whole free ammonia in the first 50 cc. of distillate. The Nessler cylinders should be made of thin colorless test tube glass, fifteen centimetres in height and twenty-three millimetres in internal diameter, with thin slightly depressed bottoms so as to stand firmly. Moulded cylinders are not satisfactory. Addition of not more than .5 cc. of Wanklyn's NH_4Cl solution, *after* the addition of Nessler solution, generally does not produce turbidity, so that an already nesslerized cylinder of deficient color may be strengthened to that extent. The colors are generally best observed by placing the cylinders on a white tile and looking perpendicularly downward, then raising them slightly and placing a second tile below at an angle of 45°, and also with deep colors by holding the two cylinders side by side against a white tile held vertically and opposite to the light. These observations, rapidly made, serve to check each other, which is especially advantageous if the liquids have become slightly turbid. But it is generally best not to attempt to estimate accurately colors deeper than that produced by about .06 mgm. NH_3 in 50 cc. water. The operator should also take the precaution to ascertain that he is free from color-blindness.

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[1] Abstract furnished by the author.

In regard to cleanliness of apparatus, directions cannot be made too emphatic. Thorough and frequent washing with ordinary good water, all apparatus, as well as the lips of the reagent bottles, immediately before actual use is most essential, and must be scrupulously performed. No other work involving the use of ammonia or its volatile compounds should be permitted in the same room during the water analysis.

As regards the reagents it is of very great importance to have the alkaline permanganate solution perfectly free from ammonia. It should be prepared with good common distilled water, and boiled actively for four or five hours, and finally made up to one litre with distilled water which has been perfectly purified from ammonia and organic matter by careful distillation with pure alkaline permanganate solution. Ordinary white stick potash may be used in commercial condition. Dissolve 200 grams KHO and 8 grams $KMnO_4$ in separate portions of water of more than one-half litre each, and pour slowly, with stirring, the former solution into the latter, but not *vice versa*. The boiling solution should not concentrate at any time much below one-half litre, otherwise loss of oxygen ensues with conversion into manganate.

It is quite unsafe to use an impure solution of permanganate and make a correction for that ammoniacal impurity.

If the Nessler solution has been made sufficiently sensitive, the *full* color with ammonia will be developed almost immediately, although amounts of from .005 to .010 mgm. NH_3 require more time than larger quantities, but not exceeding two minutes in the former case. The whole set of nesslerizings can therefore generally be completed within a very few minutes, without mechanical aids of any kind.

Peculiar odors are occasionally noticed in the distillates of free ammonia, which are probably due to unestimated volatile organic matter. To provide for such substances, if nitrogenous, it is advisable to repeat the distillation with permanganate alone on a fresh portion of the sample, preserving the ratio of one to six between the permanganate solution and the water. Prof. Remsen and Mr. Marsh, of Princeton,[1] have observed striking differences between the added free and albuminoid ammonia and the total ammonia obtained as above indicated. Haines has also analyzed a well water of which the free ammonia distillate had a strong odor of organic substance, resembling that which the water itself had when warmed, but more intense. The water contained a large amount of vegetable matter of fungoid character. Free and albuminoid ammonia were both in very large excess, but chlorine, nitrates and total solids in amounts not greater than in pure soft spring water.—(*Jour. Franklin Institute*, Nov. 1882, 342.)

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[1] This Journal, **4**, 3, 188.

On Benzenes of Different Origin.

Experiments by VICTOR MEYER show that there are some differences between benzene obtained by fractional distillation from coal-tar and carefully purified, and that obtained from benzoic acid. A short time ago Baeyer showed that benzene unites with isatin to form indophenin:

$$\underset{\text{Isatin.}}{C_8H_5NO_2} + 2C_6H_6 = H_2O + \underset{\text{Indophenin.}}{C_{20}H_{15}NO}.$$

Meyer now shows that, while this is true of the purest benzene obtained from coal-tar, it is not true of that obtained from benzoic acid, whether the benzoic acid be extracted from urine or made from resin or toluene. He shows, further, that if coal-tar benzene is treated for about ten hours with concentrated sulphuric acid on a water-bath, then washed and redistilled, it loses the power of uniting with isatin. If the benzene-sulphonic acid which is formed in the process of purification is purified and reconverted into benzene by dry distillation, the benzene which is thus obtained has the power of uniting with isatin. The purest commercial benzene loses the power of uniting with isatin if shaken for ten minutes with concentrated sulphuric acid, and also if shaken for a short time with isatin and sulphuric acid. By way of explanation of the phenomena described, three hypotheses are mainly to be considered:

1. It is possible that, in the purest benzene obtainable from coal-tar, there is a minute quantity of some foreign substance which cannot be detected by any ordinary means, and which may, something like zinc dust or aluminum chloride, exert a kind of catalytic action, rendering the ordinarily indifferent benzene susceptible to the influence of isatin.

2. The contrary supposition may also be true, viz. that the benzene from benzoic acid contains a minute quantity of some impurity.

3. Benzene from coal-tar may contain two bodies, physically and chemically very similar, which nevertheless differ in their chemical activity—the more active one combining with isatin, and being first transformed by sulphuric acid into its sulphonic acid. The less active one would then be the chief constituent of the benzene from benzoic acid.—(*Berichte der deutschen chemischen Gesellschaft*, **15**, 2893.)

Nascent Hydrogen.

D. Tommasi has for some time past been engaged in trying to determine whether the reducing properties of hydrogen, in what is called the nascent state, are due to an allotropic condition or to new thermal conditions. He has studied a large number of reductions effected by hydrogen which are usually attributed to its nascent state, such as:

Reduction of silver chloride, bromide or iodide;
" of chloric acid and the chlorates;
" of ferric chloride;
" of nitrates;
" of chloral.

The results obtained may be stated in brief, as follows:

Silver chloride, in suspension in water acidulated with sulphuric acid, was treated with sodium amalgam. The experiment was performed in the dark and lasted forty minutes. No reduction took place. Similar experiments with the same result were performed with the iodide and bromide. On the other hand, an electric current can decompose the chloride in suspension in acidulated water. The author asks how the fact can be explained that silver chloride, which resists the action of nascent hydrogen formed by the decomposition of water by sodium amalgam, can be reduced by hydrogen, also nascent, which is formed by the decomposition of water by the electric current?

A saturated solution of potassium chlorate was acidulated with sulphuric acid and then divided into two parts. One part was treated with zinc, the other with sodium amalgam. In the former there was an abundant formation of chloride, while in the latter there was no change.

A solution of potassium perchlorate was treated with, 1. zinc and sulphuric acid; 2. magnesium and dilute sulphuric acid; 3. copper sulphate and zinc; 4. sodium amalgam; and 5. zinc and potassium hydroxide, but reduction could not be effected. When treated, however, with sodium hydrosulphite, a compound which does not give off hydrogen, the perchlorate is easily transformed into the chloride: $4SO_2HNa + KClO_4 = KCl + 4SO_3NaH$. Further, this reduction is also effected by hydrogen evolved by the action of zinc on sodium bisulphite, $HNaSO_3$.

It cannot be explained why nascent hydrogen, which is formed by the decomposition of water at ordinary temperature by zinc dust, transforms potassium nitrate into nitrite, ferricyanide into ferrocyanide, reduces indigo and the iodates, but does not reduce chlorates.

Now, if nascent hydrogen is always the same thing, if its properties are inherent, it should always effect the same chemical changes, but the experiments described show clearly that the reducing power of nascent hydrogen varies according to the chemical reaction which produces it. And if the gas, in the nascent state, is endowed with stronger affinity than in the ordinary state, this is due solely to the fact that the hydrogen at the moment it passes out of a compound is accompanied by all the heat which is produced when it is set free. Hence nascent hydrogen is synonymous with hydrogen + calories.[1] Indeed, all the reductions which can be effected by nascent hydrogen can be equally well effected by ordinary hydrogen at an elevated temperature. And the reason why hydrogen, produced by different chemical reactions, has different reducing powers, is that these reactions do not develop the same quantities of heat.—(*Bulletin de la Société chimique*, **38**, 148.)

Atomic Weight of Yttrium.

The atomic weight of yttrium has been redetermined by Cleve, upon pure material which was proved to be free from terbia. As a mean of twelve experiments upon the synthesis of yttrium sulphate, he found the percentage of yttria in the latter to be 48.503, ± .0029. Hence $Yt = 88.9, \pm .027$; or, if $SO_3 = 80$, then $Yt = 89.02$. The calculations are Cleve's, including the probable errors. The last figure suggests a pretty close conformity with Prout's law.

F. W. C.

Proposed Monument to Wöhler.

A circular has been sent out by the German Chemical Society, in which contributions are requested for the purpose of erecting a monument to Friedrich Wöhler. There are special reasons why American chemists should be well represented in the list of contributors. A sub-committee will soon be formed to facilitate the collection of money in this country, and it is hoped that especially the many among us who have profited by Wöhler's instruction and to whom the memory of the Göttingen laboratory will always remain among the brightest, will promptly respond. The sub-committee will issue a circular in the course of a few weeks.

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[1] If we represent nascent hydrogen by the formula $H + \alpha$ (α designating the calories disengaged by the chemical reaction which produces the hydrogen), we have for α the following values:

$SO_4H_2 + Zn + Aq$; $\alpha = 38$ cal.
$SO_4H_2 + Cd + Aq$; $\alpha = 23.8$ cal.
$SO_4H_2 + Mg + Aq$; $\alpha = 112$ cal.
$2ClH + Zn + Aq$; $\alpha = 34.2$ cal.
$2BrH + Zn + Aq$; $\alpha = 34.2$ cal.
etc. etc.

As we see, the value of α varies for each chemical reaction, and consequently the hydrogen will be the more active the greater the value of α. For sodium amalgam α would be equal to about 112 cal.

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